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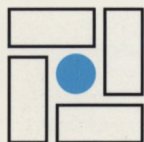
LITHOLOGY AND MINERAL RESOURCES

Official English Translation of *Litologiya i Poleznye Iskopaemye*

Editor-in-Chief
Vladimir N. Kholodov

Academician of the Academy of Natural Sciences
Professor, Dr. Sci. (Geol.–Miner.)

**A Journal on Problems of the Theory of
Sedimentary Rock Formation and Ore Genesis**



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Lithology and Mineral Resources

(*Litologiya i Poleznye Iskopaemye*)

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Lithology and Mineral Resources (Litologiya i Poleznye Iskopaemye) reviews a wide range of problems related to the formation of sedimentary rocks and ores. Special attention is devoted to comparison of ancient sedimentary rock and ore formation with present-day processes, as the idea of actualism has always constituted one of the bases of the scientific philosophy of lithologists. A major part of the journal is devoted to comparative analysis of sedimentary processes on continents and in oceans, as well as the genetic aspects of the formation of sedimentary and hydrothermal-sedimentary mineral resources. The journal was founded in 1963 by Academician N. M. Strakhov. It will be of interest to lithologists, petrographers, geochemists, mineralogists, ore geologists and metallogenists, as well as to other geologists, ecologists, researchers of experimental and analytical laboratories, and graduate students.

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Biochemogenic Genesis of the Glauconite–Nontronite Series Minerals in Present-Day Sediments of the Pacific Ocean

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Abstract—Based on detailed mineralogical investigations of glauconite grains, coprolites, and host components, the process of glauconite formation in present-day sediments of the Northeast Pacific Basin near the Mexican coast is examined. Glauconite grains are formed *in situ* in intensely bioturbated sediment in several stages. The role of the biogenic factor in the formation of the glauconite–nontronite series grains and the influence of bacterial activity upon glauconite formation, in particular, are described. It is assumed that certain fragments of nanostructures in coprolites and glauconite grains can be fossilized by bacterial colonies at early stages of glauconitization.

INTRODUCTION

The green globular dioctahedral 2 : 1 phyllosilicates in marine sediments of different lithological types and ages are characterized by a wide range of structural and crystallochemical features. They form continuous isomorphic series ranging from smectites to mixed-layer phases and micaceous minerals. Micaceous minerals are represented by the Fe³⁺–Mg- and Fe³⁺–Al-bearing varieties. The Fe³⁺–Mg-bearing varieties make up solid solutions ranging from glauconite to celadonite, whereas the Al₂O₃-bearing varieties form varieties ranging from glauconite to Al-glauconite and illite (Drits and Kossovskaya, 1985, 1991; Drits *et al.*, 1993; Ivanovskaya, 1994, 1996; Lipkina, 1987; Lisitsina *et al.*, 1976; Odin, 1975; Shutov *et al.*, 1972; Tsipurskii and Ivanovskaya, 1988; and others).

Present-day sediments of shelves and continental slopes of the World Ocean incorporate green grains composed of glauconite–celadonite minerals and their mixed-layer varieties. According to the classification in (Drits and Kossovskaya, 1985), these formations are referred to as the genetic group of ferruginous micaceous minerals in oceanic coastal zones with a prevalence of sedimentary glauconites and the occasional presence of hydrothermal glauconite–celadonite varieties. Lipkina (1980) detected Fe-rich micaceous minerals in the present-day volcanic edifices and erosion products in the Sea of Japan. Subsequently, Drits *et al.*, revealed that the micaceous minerals are mostly represented by celadonites rather than glauconites, as was assumed by Lipkina, while the glauconites proper, which form an isomorphic series with celadonites, are rarer and generally have a tetrahedral charge similar to its upper limit in celadonites (Lipkina *et al.*, 1987). Lipkina concluded that the morphological and chemical features of minerals in sediments of the Japan Sea are akin to those of the Northwest Pacific glauconites studied by Lisitsina *et al.* (1974).

Based on an overview of the glauconite study in bottom sediments from the Pacific coastal zone from Japan to Mexico, Lisitsina and Butuzova (1981) assumed that oceanic glauconites are authigenic formations (Lisitsina *et al.*, 1974, 1976). They were originated in the diagenesis zone, and the continent-derived material served as the source of construction components. Logvinenko (1980) and Nikolaeva (1977) believed that the major part of glauconite grains in coastal sediments is terrigenous.

Odin (1975) supposed that glauconitization occurs in the grain substrate (in nuclei of microfaunal remains, coprolites, as well as biogenic carbonate and mineral fragments), among which the most favorable ones are represented by large (0.5 mm) porous varieties on the floor of an open marine basin with a suppressed terrigenous sedimentation. The central part of grains is characterized by the development of a semiisolated (from seawater) environment that prompts the crystallization of Fe-bearing phyllosilicates. Gradually, the outer zone is also subjected to recrystallization.

With respect to crystal chemistry, glauconitization proceeds in four stages. At stage 1, either the substrate is replaced by neomorphous microcrystals of smectite or glauconite–smectite (K₂O 2–4%), or these minerals grow upward and infill voids. At stages 2–4, the entrapment of K by the swelling silicate structure results in the gradual transformation of mixed-layer minerals into glauconite. Simultaneously, the inherited ⁴⁰Ar is gradually lost. At the end of stage 4, the well-crystallized glauconite (K₂O >7%) is formed and the ⁴⁰Ar release is terminated. According to estimates of Odin *et al.*, the duration of glauconite formation at the sedimentary stage varies from 100 ka to 1 Ma (Odin and Matter, 1981; Odin and Dodson, 1982; Odin and Fullager, 1988). These researchers considered that the overestimated dating of glauconite minerals in the

present-day oceanic sediments is provoked by an incomplete glauconitization of the older mineral, in which the radiogenic ^{40}Ar heritage is still retained.

Lisitsina and Butuzova (1981) also considered that the overestimated isotopic age of present-day oceanic sediments cannot serve as evidence of the terrigenous origin of glauconite, because the latter contains an admixture of the K-bearing matrix. Logvinenko (1980) and Nikolaeva (1977), however, held the opposite viewpoint. They attempted to substantiate the clastic origin of glauconite by K–Ar age estimates (2–20 Ma), in addition to mineralogical criteria. The K–Ar data were obtained for glauconite samples from sand and mud in different areas of the Pacific and the Hole 670 sample (1.8 Ma) collected from the 200–214 cm interval. One of our samples is also collected from this borehole but at a higher level (150–165 cm).

Like Odin, Clauer *et al.* (1992) considered that the neogenic glauconite indicates the sedimentation timing, but the mineral is formed by a different mechanism. Based on Odin's crystallochemical model, they assumed that the first stage of dissolution and recrystallization of terrigenous clay particles into glauconite minerals proceeds in a closed sedimentary environment without the participation of seawater (they probably bore in mind the initial diagenesis zone, but did not indicate it). The second stage of glauconitization starts when the K_2O content is equal to 4.5%. This process is accomplished at seafloor. At $\text{K}_2\text{O} > 6.5\%$, the terrigenous material is completely reworked, and its isotope memory disappears. As is well known, the contact of glauconite minerals with seawater leads to certain crystallochemical changes in their structure; e.g., the partial oxidation of Fe^{2+} and loss of K_2O (Murav'eva *et al.*, 1985). Therefore, the opinion of Clauer *et al.*, is not sufficiently persuasive. The same conclusion is valid in the case of Odin's model, because one can hardly imagine a favorable environment for glauconite formation in grain substrate that rested on seafloor for 1 Ma.

We studied present-day glauconite sediments from the Mexican sector of the Pacific and attempted to elucidate the problem of glauconite formation *in situ*, as well as some other genetic problems, including the role of the biogenic factor in glauconitization.

This work is based on the comprehensive mineralogical study of glauconite grains, coprolites of various grades of mineralization, and terrigenous matrix, as well as their interrelations. The relationship between glauconite grains and different components of host sediments has been reported by several researchers (Hughes and Whitehead, 1987; Lisitsina *et al.*, 1974; Lisitsina and Butuzova, 1979, 1981; and others). However, this aspect has not been specially studied by lithologists and mineralogists.

The green grains studied are represented by 2 : 1 phyllosilicates that form a continuous structural-isomorphic series ranging from mixed-layer glauconite–nontronite minerals to the glauconite composition

illites and glauconite proper (dioctahedral Fe^{3+} -bearing mica). However, we use the term glauconite or glauconite grain in general description, and the structural variety is only indicated wherever essential. It is worth mentioning that researchers use different terms, such as pellets, pelloids, globules, microconcretions, etc., for designating glauconite formations. Since the green segregations (except coprolites that constitute ~1 wt %) in samples studied are generally characterized by irregular forms, we label them as glauconite grains.

GEOLOGICAL SETTING OF THE OBJECTS STUDIED

Present-day sediments of the Northeast Pacific Basin were picked up in the Mexican coast area (Fig. 1) near Manzanillo (samples 8281, 8253, and 82100) and Mazatlan (sample 670). The Manzanillo samples were provided by A.I. Voznesenskii (8th cruise of R/V *Akademik Nikolai Strakhov*, 1989), and the Mazatlan samples were presented by N.A. Lisitsina (9th cruise of R/V *Dmitrii Mendeleev*, 1973).

Site Manzanillo. Here, the samples were collected by a grab sampler from sediments on the continental slope (samples 8281 and 8253) and oceanic slope (sample 82100) of the Middle America Trench. In the middle zone of the continental slope, the glauconite-bearing sediments were encountered on flattened rises separating canyons and basins. According to Voznesenskii, these sediments represent oxidized, brownish gray or greenish, sandy (to a variable extent), poorly sorted, clayey–silty muds with detritus, pellets, or gravel of indurated clays or native tuffogenic rocks. They were characterized by strong bioturbation and an abundance of coarse sand-size glauconite microconcretions. The thickness did not exceed 1–2 m (Voznesenskii, 1994, p. 102).

Sample 8281 (coordinates $18^\circ 21'$ and $104^\circ 01.4'$) was picked up at a depth of 1407 m (interval 5–30 cm). The sediment is characterized by dark gray and dense, clay- and sand-rich, obscure-laminated mud with numerous glauconite grains, coprolites, as well as siliceous and carbonate organic remains. The values of Eh and pH are equal to +120 mV and 7.29, respectively.

Sample 8253 ($18^\circ 34.1'$ and $104^\circ 18.4'$) was collected from sediment at a depth of 1600 m. It is similar (in composition and structure) to sample 8281, but the glauconite content is appreciably lesser. The geochemical parameters are as follows: Eh +60 mV; pH 7.44.

Sample 82100 ($17^\circ 50.4'$ and $104^\circ 43.8'$) was picked up from the 5–25-cm-interval of core recovered from a depth of 2860 m. It is represented by greenish gray, dense, fine silt-size, sand-poor, nonlaminated mud with rare glauconite grains, numerous coprolites, and micro-organism remains.

Site 670 is located on the south of the Gulf of California, within the 668–671 profile extending from the Cape Mazatlan toward the open ocean (Fig. 1). Sam-

ples at Site 670 (depth 145 m, coordinates 22°36.3' and 107°24.5') were collected by a gravity corer from the 150–165 cm interval with the minimum Eh value (–350 mV) and a slightly higher pH value (7.5) (Volkov *et al.*, 1976).

Detailed and general characteristics of sediments from sites 668–671 are given in several publications (Lisitsina *et al.*, 1976; Rozanov *et al.*, 1976; Volkov *et al.*, 1976). The most essential information concerning the scope of this work is presented below.

The open Pacific floor is covered with deep-water red clays. Over a distance of 800–1000 km from the Mexican coast, red clays are replaced by hemipelagic and coastal muds. The sediment typification here is akin to a counterpart in the northwestern sector of the Pacific (Lisitsina and Dvoretzskaya, 1972). Coastal sediments of the shelf and continental slope (sites 668–670) are represented by clayey mud with an admixture or interlayers of glass, terrigenous grains, siliceous and carbonate organisms, fragments of Pelecypoda and Gastropoda shells, etc. Diagenetic formations (sulfides and glauconite), which are typical for coastal and hemipelagic sediments, and free H₂S are ubiquitous. The C_{org}-rich (1.0–6.3%), coastal and hemipelagic, reduced muds are responsible for the development of a reduced sediment belt around the ocean (Strakhov, 1972 and others).

Glauconite is irregularly distributed at sites 668–670. Its content is negligible at sites 668 and 669. At Site 670, glauconite globules are pervasive, but their content varies from fractions of percentage to 49 vol %. The maximum concentrations are confined to muds enriched in the sandy-silty material (Lisitsina *et al.*, 1976).

STUDY METHOD

The samples were examined for the following components: (1) glauconite grains, (2) host matrix, (3) beige-colored grains, and (4) coprolites. They were analyzed by an application of conventional optical methods and scanning electron microscopy (SEM). In the Manzanillo samples (8281, 8253, and 82100), grains were extracted from the indurated clayey mud by the following procedure. After soaking and washing the stiff mud, it was dried under a lamp, screened through sieves, and then subjected to short-period (15–30 s) ultrasonic processing that made it possible to destroy the matrix and purify grains. The grains were finally purified under a binocular microscope, separated into different-density fractions (sample 8281), and then studied by X-ray analysis and microprobe (Camebax) methods. Simultaneously, the matrix (sample 670) or clayey fractions (samples 8281, 8253, and 82100), which were extracted from the sediment, were studied by the XRA method.

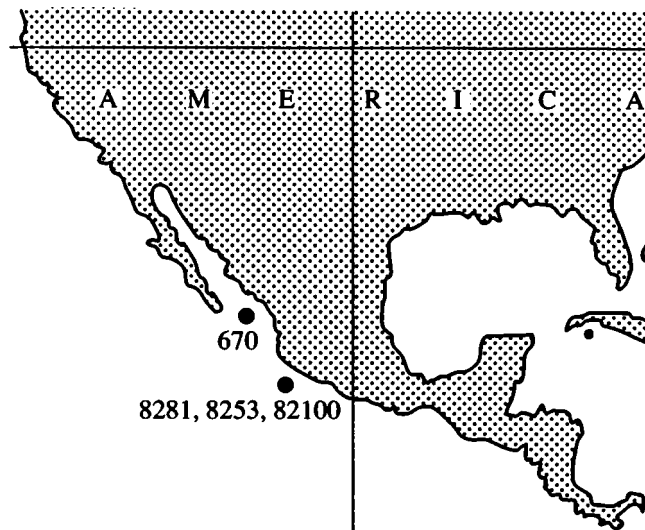


Fig. 1. Sample location.

Sample 670,¹ which is represented by silty sand, was presented to us in a clay-free state. Only a few grains of stiff matrix were preserved. After screen-washing the sediment, glauconite grains from each fraction were separated from terrigenous components with the help of an SIM-1 electromagnetic separator and then divided into different density fractions that were subsequently examined by X-ray microspectral analysis (Camebax), chemical method (whole-rock microanalysis), X-ray analysis, and scanning electron microscopy.

The X-ray characteristics of samples (content of swelling layers, parameter *b*, and lattice defect) were ascertained on the basis of the analysis of diffractograms of oriented and nonoriented specimens, according to the procedure proposed by Drits *et al.*, (1993). The X-ray and microprobe analyses were performed by E.V. Pokrovskaya and G.V. Karpova, respectively. The SEM analysis was conducted in cooperation with N.V. Gor'kova (GIN).

CHARACTERISTICS OF ROCKS

Like glauconite grains, coprolites represent a typical component of the sediments studied. The different grades of their mineralization (glauconitization) deserve detailed consideration.

The average size of coprolites varies within 0.16–0.4 mm. Larger (sample 8281) and smaller coprolites are subordinate. The shape is generally ellipsoidal and sometimes rounded. In samples 8281, 8253, and 670, coprolites reveal a gradual change in color from pale brown and beige to pale green and dark green. Their density also varies from 2.2–2.5 g/cm³ for the light-colored varieties to 2.5–2.65 g/cm³ for the rare dark-colored ones.

¹ Henceforth, the term "station" is substituted by "sample."

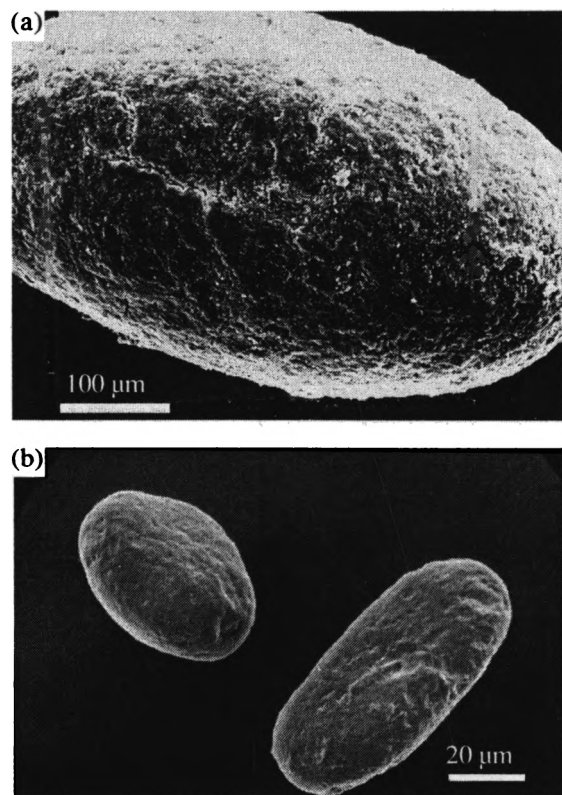


Fig. 2. Surface of coprolites: (a) present-day (sample 8281), (b) Precambrian (sample 60, Riphean sediments of the Southern Ural, collection of T.A. Ivanovskaya, SEM image).

The surface of coprolites is also variable. It is homogeneous and devoid of cracks in the pale brown variety. The beige and pale green varieties contain a network of shallow cracks infilled with a pale microgranular material (Fig. 2a). The network of deep cracks in the dark green variety is also infilled with a pale material. In terms of color, shape, and surface type, green coprolites are akin to ellipsoid glauconite globules, which are well known in both present-day and ancient sediments, including the Precambrian ones (Fig. 2b). The specific features of coprolites are described below in the section devoted to their study under the scanning electron microscope.

In sample 82100, the major part of coprolites is similar to the matrix in color, and only a few aggregations have the pale green color. Additionally, the sample contains abundant isometric grains. The color of these grains is similar to that of the matrix, but sometimes beige and pale green varieties, which are slightly more massive than the matrix, are also encountered.

Glauconite is abundant in sample 8281, subordinate in 8253, and rare in 82100. It has similar color, shape, and other physical properties in all of the three samples. In each sample, the color varies from pale green to dark green. The size generally varies from 0.1

to 1.0 mm. Larger (0.4–1.0 mm) grains are widespread in sample 8281 and insignificant in sample 8253. The density of glauconite in the 0.2–0.6 mm fraction from sample 8281 ranges between 2.4 and 2.65 g/cm³. The dominant fraction is represented by grains with density 2.45–2.6 g/cm³, as is evident from the following density fraction distribution (%): 2.4–2.45 (11), 2.45–2.5 (29), 2.5–2.55 (32), 2.55–2.6 (26), and 2.6–2.65 g/cm³ (~2). The lightest (2.2–2.4 g/cm³) fraction consists of a few beige to pale green glauconite grains, coprolites (pale brown, beige, and light green), and matrix.

The shape of glauconite grains is mostly irregular. Globular varieties (rounded, oval, and ellipsoid) are rare. The grain surface is generally uneven and either partly or completely covered with a pale to white material, which is resistant to ultrasonic processing. The surface is decorated with different (in depth and width) cracks that are open or infilled with a varicolored (white to pale green and dark green) substance.

The study of thin sections has revealed a strong structural heterogeneity of glauconite grains. They incorporate different (in green color shades and structure) patches and rims, as well as numerous clastic and biogenic inclusions that are similar to inclusions in the host sediment (Fig. 3). Inclusions are represented by fragments of various minerals, volcanic glass, diatom frustules, radiolarian shells, and other sedimentary components. All of them are dissolved to a variable extent and replaced by glauconite. A similar process is ascertained in inclusions, which are scattered in pale green rims around dark green grains, and large intricate cracks infilled with a pale green material. Occasionally, such cracks almost crosscut glauconite grains.

The subordinate, dark green clastic grains are covered with a pale green shell that often obliterates the acute edges and faces of grains (Fig. 3f). The matrix in rims of such grains is occasionally bleached. Additionally, one can observe the encapsulation of a glauconite grain by another grain, as well as terrigenous or organic mineral fragments enclosed partly in glauconite grains and partly in matrix (Figs. 3a, 3d).

Sample 670. The mineralogical features of glauconite grains from different levels of Site 670, and other sites located near the Mexican coast, have been described earlier (Lisitsina *et al.*, 1976; Lisitsina and Butuzova, 1979). According to these researchers, the shape of glauconite grains and their relationship with host mud, as well as their distribution in the sedimentary pile (the mottled structure and the absence of direct relationship with lamination) are evidence for the diagenetic origin of glauconite in the reduced sediment zone of the Northeast Pacific Basin.

Since the above-described physical properties (morphology, color, dimension, heterogeneity, etc.) are valid for the sample 670 grains, we shall dwell on the comparison of different density fractions of this sample. The density varies from 2.2 to 2.8 g/cm³. The heaviest fraction (2.75–2.8 g/cm³) constitutes less than 1%. In

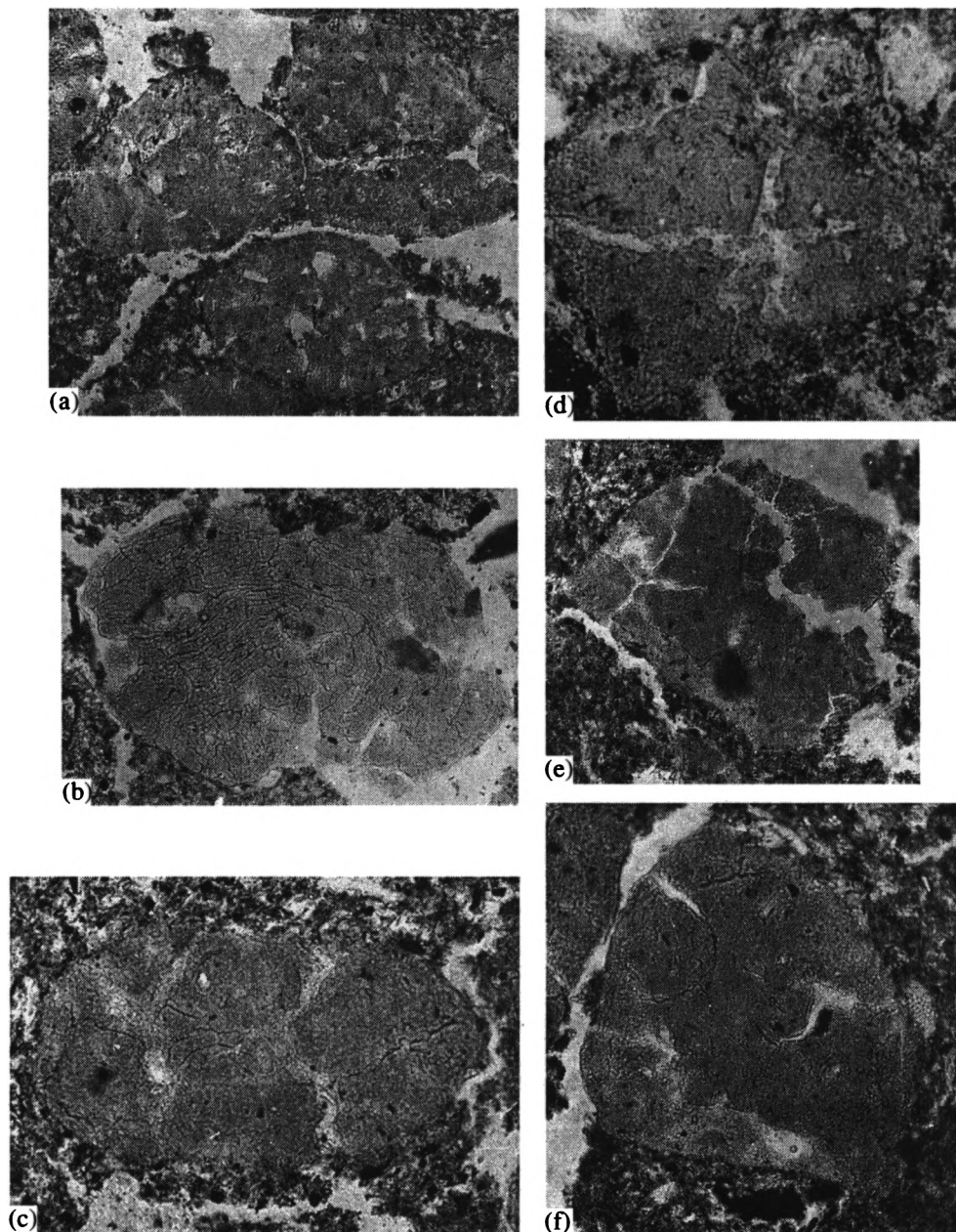


Fig. 3. Microstructure of glauconite grains, present-day sediments (sample 8281, microphotographs of thin sections, magn. ~65. (a) Glauconitized coprolites with a silty terrigenous material (the encapsulation of one glauconite grain by another one is seen in the upper part); glauconitized coprolites with: (b) typical "snow lump" microstructure, (c) cracks infilled with pale-colored clayey material; (d) glauconite grain crosscut by open cracks infilled with pale-colored clayey material (a radiolarian shell partly included in the grain can be seen in the upper part); (e, f) glauconite grain fragments (dark green in thin section), in which the uneven crack is infilled with pale green clayey material.

coarser (0.315–0.4 and 0.4–0.63 mm) fractions, grains with a density maximum (2.6–2.7 g/cm³) are predominant, while light (<2.55 g/cm³) grains are insignificant (8–10%). Correspondingly, light grains are abundant (~28%) and heavy (2.6–2.7 g/cm³) grains are subordinate in the fine (0.2–0.315 mm) fraction (Fig. 4).

The color differs from beige in light fractions to pale green and dark green in heavy fractions. The light

(<2.5 g/cm³) fraction contains numerous pale brown, beige, and pale green coprolites that are glauconitized to a variable extent and can be divided (in color and surface type) into varieties similar to those in samples 8281 and 8253. Dark-colored coprolites are rare in heavier fractions. Additionally, both light and heavy fractions of the sample studied contain irregular grains along with nuclei of foraminifera and other organic remains. Pale green and dark green grains are crosscut

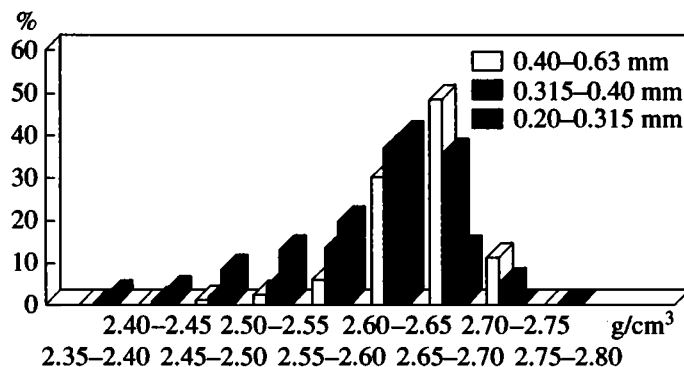


Fig. 4. Histogram of grain distribution in density (sample 670).

by cracks that are open or infilled with a pale substance. Several grains are coated with a white or pale green and fine-grained material.

Thus, the glauconite grains from sample 8281 (the most representative sample from Site Manzanillo) and sample 670 are very similar in physical properties, except for some differences in color shades and density characteristics. For example, sample 8281 grains have a lesser density (2.45–2.6 g/cm³), relative to sample 670 grains (2.55–2.75 g/cm³).

NANOSTRUCTURE STUDY

Scanning electron microscopy was applied to the following objects: (1) coprolites of different (pale brown, beige, pale green, mottled, and zonal) colors (samples 82100, 8281, and 670, size 0.2–0.6 mm, density <2.45 g/cm³); (2) pale green foraminiferal nuclei (sample 670, 0.315–0.4 mm, 2.4–2.45 g/cm³); (3) green glauconite grains (sample 8281, 0.2–0.6 mm, 2.45–2.6 g/cm³; sample 8253, 0.2–0.4 mm); and (4) pale green to dark green grains with different density values (sample 670, 0.1–0.63 mm, 2.45–2.7 g/cm³). In addition to the examination of the surface and shear joints in these objects, we also investigated the host (pale brown) matrix (sample 8281, 0.4–0.63 mm). While studying the surface of coprolites and glauconite grains, we paid special attention to the nanostructure of the white clayey cement in cracks and, additionally, to the composition of partial or complete coating of glauconite grains (sample 8281).

The SEM investigation of the highly porous matrix is a complicated procedure. Small authigenic clayey flakes were occasionally detected in the pore space and at the surface of some terrigenous fragments. Terrigenous fragments and bioclasts are pervasive in the matrix.

Pale brown coprolites have a lesser porosity and a higher density owing to the increased content of clayey flakes. The content of the mineral and organic fragments (radiolarians, diatom algae, etc.) is high but relatively less so than in the matrix. Organic remains are

encountered in not only the interior but also in exterior zones of coprolites. In the latter case, remains are strongly disintegrated and replaced by clayey flakes to a variable extent. Occasionally, coprolites include patches of pyrite microcrystals.

Beige-colored coprolites can be subdivided into two groups differing in morphology and surface type. The first group includes coprolites with a well-developed egg-shaped or ellipsoid morphology and a smooth surface crosscut by a network of fine closed cracks. The cracks are slightly opened in only few of the larger species. The cavities within the rough and crenulate crack edges are hollow (Fig. 2a). The second group includes beige and mottled coprolites with small green patches in the interior and exterior zones. These coprolites have a rough (hummocky) surface owing to the presence of some flat or slightly convex green patches (Fig. 5). The patches have a specific nanostructure (Fig. 5d) and are separated by wide but shallow cracks with uneven or rounded edges (Figs. 5a–5c). The cracks are infilled with matrix and authigenic clayey flakes. In the thin section, the clayey material is colorless or pale green. The comparative SEM analysis of the morphology and surface type in two groups of coprolites reveals that the hummocky variety with a network of wide cracks has a brain-shaped nanostructure (Figs. 5a, 5b).

Pale green coprolites can also be subdivided into two groups similar to the beige coprolites in physical properties; e.g., the brain-shaped nanostructure is observed in the second group. The content of organic and mineral fragments is reduced in the beige and pale green coprolites, relative to the pale brown variety.

As was mentioned above, in contrast to the matrix, the pale brown coprolites contain a greater amount of compact clayey flakes (Fig. 6a). Generally, the flakes are obscure under the microscope, but sometimes discernible patches are also observed. In the latter case, the flakes make up a cellular nanostructure typical of both the beige and the pale green varieties, in which the content of authigenic clayey flakes is sharply increased. The flakes make up walls of cells with different (in shape and size) orifices in between. Based on the cell

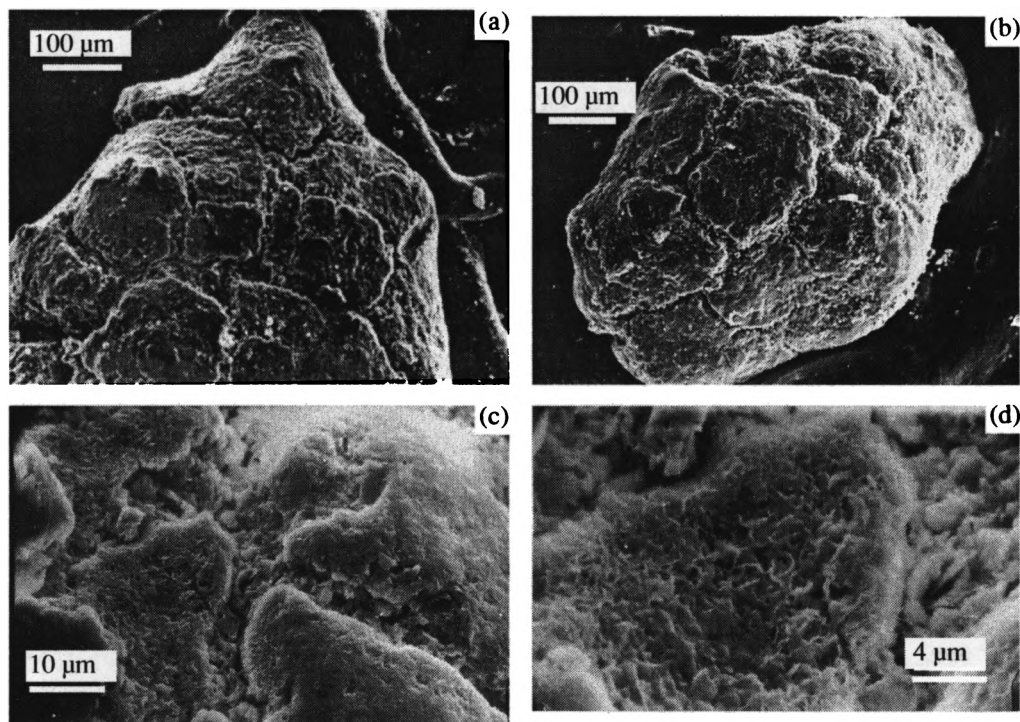


Fig. 5. Coprolites with a hummocky surface crosscut by wide cracks (SEM images). (a, b) Coprolites with the specific brain-shaped surface; (c, d) nanostructure manifestation on surface and in cracks.

size, we can tentatively identify two types of nanostructure: (1) the fine-cellular ($<0.5\ \mu\text{m}$) type and (2) the coarse-cellular ($1.0\text{--}2\ \mu\text{m}$) type and the transitional type as well (Figs. 6b, 6c). The type 2 flakes are characterized by a greater size ($1\text{--}2\ \mu\text{m}$). In some places, one can observe accumulations of different-size flakes in the form of irregular clusters (Fig. 6d) and rounded (or oval) microglobules (Figs. 7a, 7b). The microglobules range from 1 to $3\ \mu\text{m}$ in size. The shear joints reveal that microglobules can be composed of an indurated homogeneous material (Fig. 7c). Their surface is decorated with an intricate network of fine, clay mineral film (petals) (Fig. 7d). Microglobules are irregularly distributed. They are particularly widespread where fragments of diatom frustules and radiolarian shells are replaced by clayey material (Fig. 7a).

A similar structure (with microglobules covered by fine petals) is detected in some sectors of the foraminiferal nucleus fragments. In zonal-colored or mottled coprolites, the varicolored (pale brown, beige, and green) zones and sectors have a similar cellular nanostructure. However, sometimes the clay minerals in green sectors make up a specific nanostructure characterized by the accumulation of curved or straight vermicular bodies, up to $0.17\text{--}0.2\ \mu\text{m}$ in size. The patches also include compact microglobules with a diameter of about $1.5\text{--}2\ \mu\text{m}$ (Figs. 7e, 7f). We consider this nanostructure as a biomorphic aggregate. It should be noted that a highly similar structure was detected in Al-glaucconite from the nucleus of Chancelloriidae (Geptner *et al.*,

1994). During an active life period, the voids in Chancelloriidae were infilled with an organic tissue that served as a favorable substrate for the development of microorganisms after the death of animals.

The pale green grains and coprolites, have a similar nanostructure, i.e., coarse- and fine-cellular structure formed by the accumulation of different-size flakes. Based on the study of the present-day and Cenozoic glauconite-bearing sediments, Odin has also reported the structural similarities of green coprolites and glauconite grains with $\text{K}_2\text{O} < 7\%$ (Odin, 1971, 1974, 1975).

The green grains have both similar and distinct nanostructural features, relative to the above-described structural features. For example, they are characterized by the cellular structure, but they also include some compact sectors noted by a random distribution of fine ($<0.5\text{--}1.5\ \mu\text{m}$) flakes. The latter version, demonstrated in Fig. 6e, represents a transitional (with respect to the typical glauconite-type) structure that has been reported by us and other researchers (Geptner *et al.*, 1994; Lisitsina and Butuzova, 1981; Odin, 1971, 1974, 1975; and others). In the K-rich ($\text{K}_2\text{O} > 7\%$) glauconite, large (up to $5\text{--}10\ \mu\text{m}$) flakes are generally random-oriented, smoothly curved, and sometimes clustered as fan-shaped aggregates (Fig. 7g). This type of structure, noted in globules of the dioctahedral $2:1$ phyllosilicates in the Cenozoic to Precambrian sediments, does not depend on the mineral composition (glauconite, Al-glaucconite, or illite). For example, Fig. 7h shows a

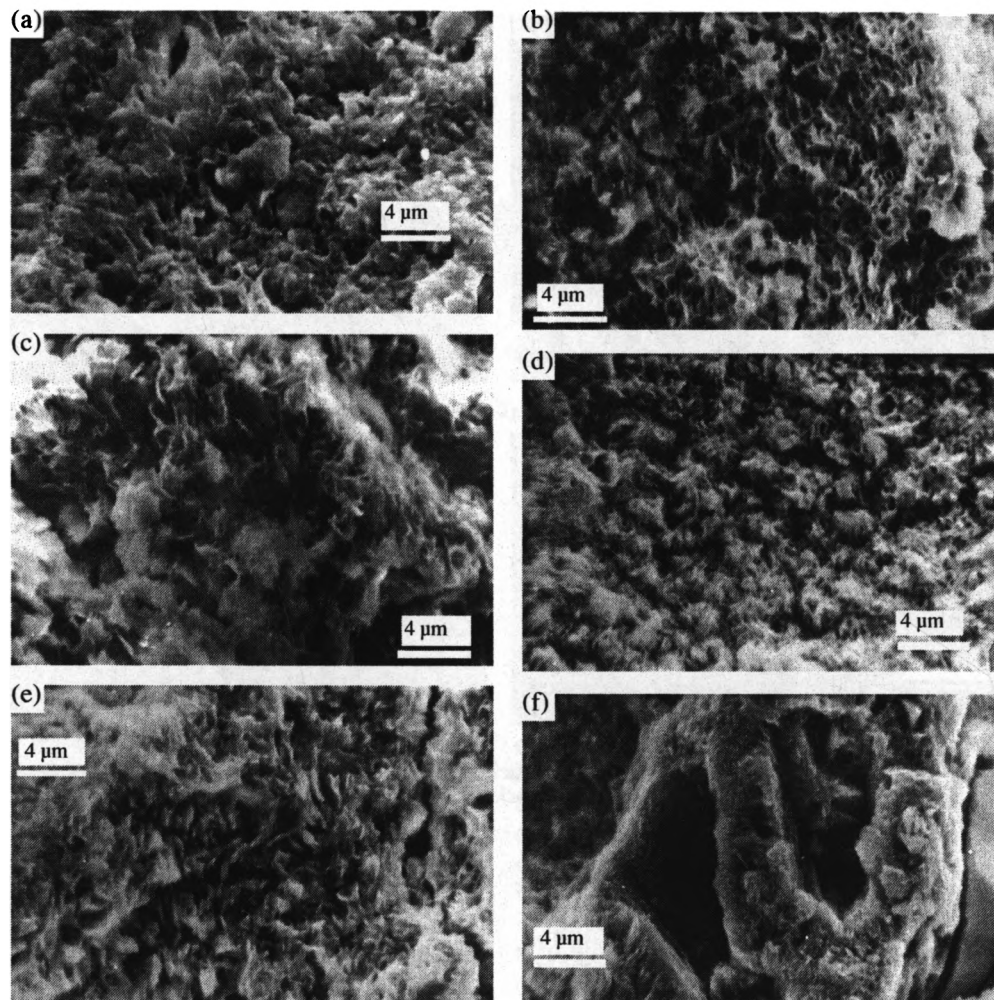


Fig. 6. Types of nanostructure. (a–d) Beige-colored and pale green coprolites; (e, f) glauconite grains. SEM images.

globule nanostructure (sample 60, see also Fig. 2b) composed of illite (K_2O 8.76%).

In addition to the above-described nanostructure modifications, a crustification type is also observed in clastic green grains (with frequent traces of dissolution) that are surrounded by rims of tightly packed fine-oriented flakes (Fig. 6f). It is worth noting that the light-colored crust and interior zone of the majority of green grains in sample 8281 are characterized by a combination of sectors with cellular and more compact (intricate flaky) nanostructures.

THE X-RAY DATA

An analysis of diffractograms of oriented and powder specimens of the pale brown matrix and clayey fractions (<0.005 and <0.05 mm) extracted from samples 8281, 8253, 82100, and 670 showed that they consist of major Al-smectite ($b = 8.94$ – 9.00 Å), subordinate dioctahedral illites and chlorite, minor feldspars, and rare quartz (plus calcite and zeolites in sample 670).

This can be illustrated by diffractograms of oriented specimens and the $d(060)$ -region powder diffractogram of sample 8281 (Fig. 8). Analogous diffraction features were detected in this sample for pale brown coprolites as well.

Based on diffraction features of oriented specimens, brown coprolites (sample 8281, 0.2–0.6 mm, 2.3 – 2.4 g/cm³) and irregular grains with analogous physical properties (color, size, and density) are represented by mixed-layer micaceous smectites with an irregular quantitative relationship between the smectite- and mica-type interlayers in individual particles of the material. On the whole, the smectite component (60–70%) prevails in the structure. The dioctahedral illite, chlorite, and feldspars are present as subordinate components. Quartz is present as a rare mineral.

The diffraction characteristics of green grains (0.2–0.63 mm) from sample 8281 are as follows. As opposed to beige coprolites, the pale green varieties (density 2.35 – 2.45 g/cm³) are composed of mixed-layer minerals with a depleted content of smectite layers (~ 30 – 60%).

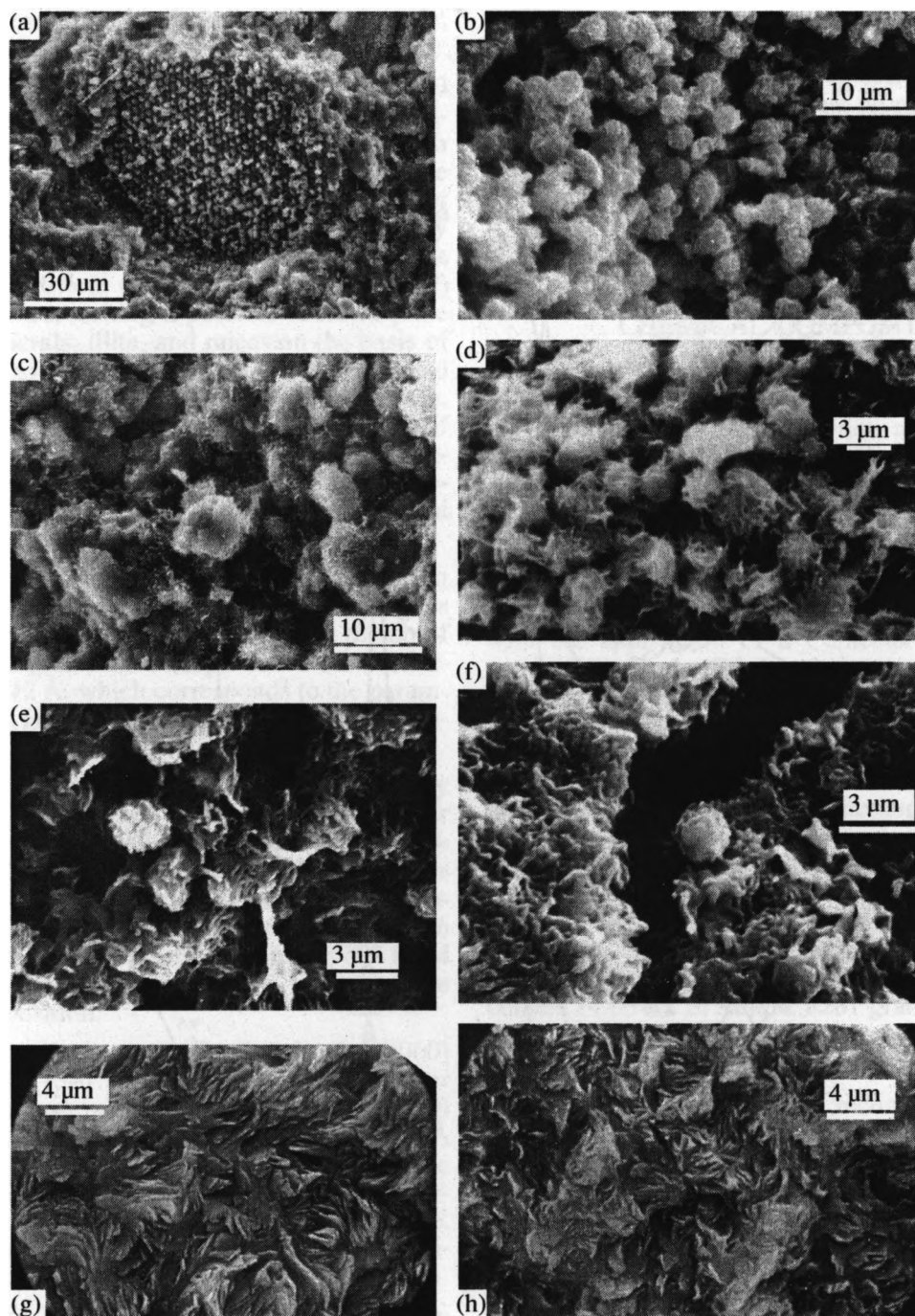


Fig. 7. Types of nanostructure in varicolored coprolites and the glauconite–illite series grains. (a–f) Present-day sediments (samples 8281, 82100); (g) Paleogene, Crimea, collection of T.A. Ivanovskaya (sample 5, K_2O 8.40%); (h) Precambrian (sample 60, K_2O 8.76%). SEM images.

The dark green varieties ($2.45\text{--}2.6\text{ g/cm}^3$) consist of illites with swelling layers up to 15–25% (Fig. 8). As is evident from the figure, diffractograms of oriented illite specimens have a prominent diffuse background in the low-angle region, while diffractograms of the mixed-layer minerals are noted by the presence of blurred reflections and the appearance of a wide diffuse band

($4\text{--}5^\circ 2\theta$) that hampers the precise interpretation of the XRD data.

In samples 8253 and 82100, the green grains are composed of mixed-layer minerals, in which the swelling layers constitute about 30–40%. In sample 82100, the irregular beige grains, which dominate over the green ones, are represented by smectite; dioctahedral

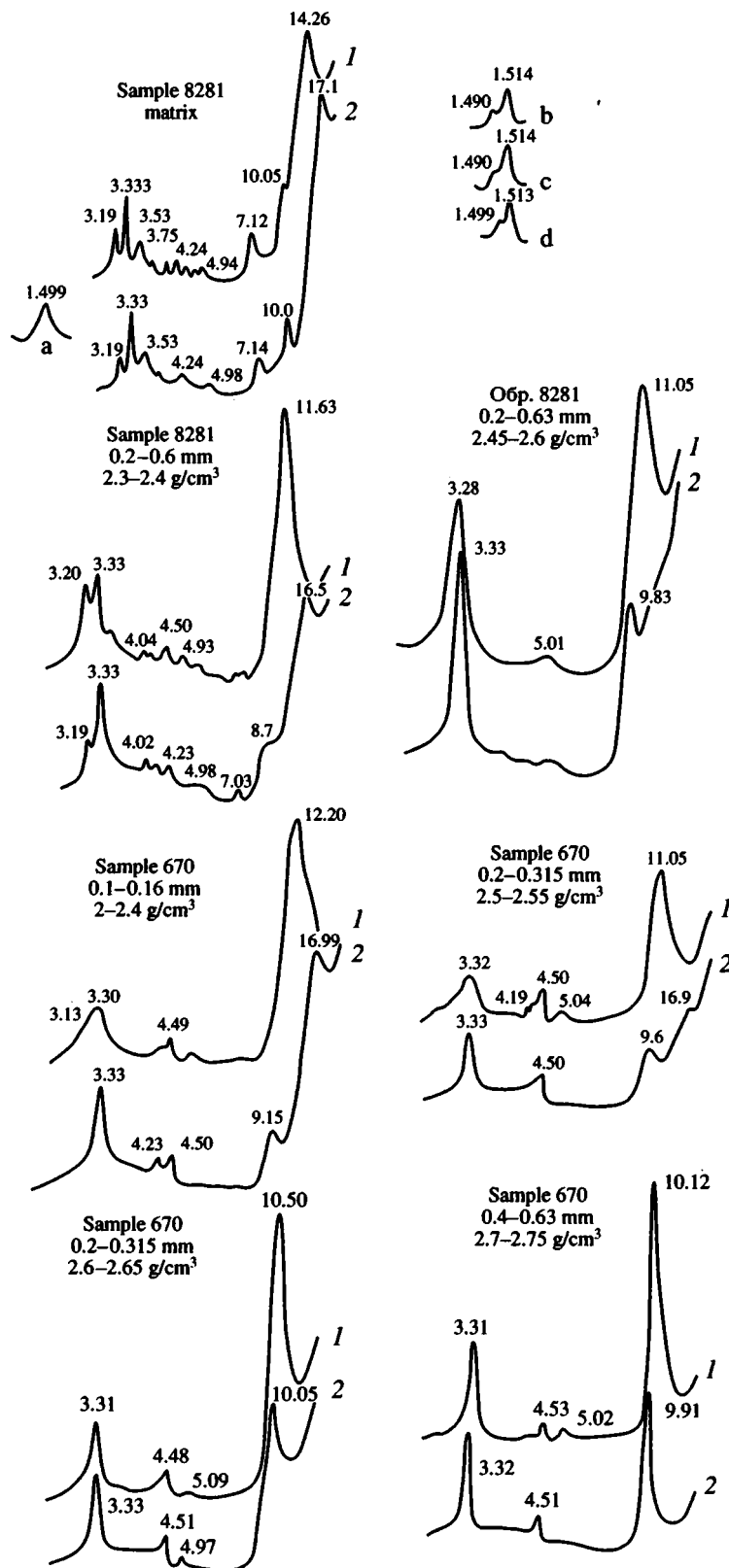


Fig. 8. Diffractograms of samples 8281 and 670. Oriented specimens: (1) in air-dry state; (2) ethylene glycol-saturated. Powder specimens, d(060) region: (a) sample 8281 (matrix); (b) sample 8281 (0.2-0.63 mm, 2.45-2.6 g/cm³); (c) sample 670 (0.2-0.315 mm, 2.4-2.45 g/cm³); (d) sample 670 (0.4-0.63 mm, 2.7-2.75 g/cm³).

illite and chlorite are found as the subordinate minerals; and feldspars and quartz are rare.

Like the sample 8281 counterparts, sample 670 grains with a green color of various shades are composed of the dioctahedral 2 : 1 phyllosilicates, in which the relationship between the micaceous and smectite layers depends on the density of grains (Fig. 8). For example, the content of swelling layers gradually decreases from 50% in the light (2.2–2.4 g/cm³) pale green grains to <10% in the heavier (2.7–2.75 g/cm³) dark green varieties, making it possible to identify the mixed-layer minerals, illite, and micas on the basis of the content of swelling layers (25–50, 10–25, and <10%, respectively). Like the sample 8281 curves, sample 670 diffractograms of oriented specimens of illites and mixed-layer minerals contain a diffuse background that reduces the resolution of the first and second basal reflections. However, the diffuse background is considerably stronger in sample 8281.

The analysis of powder diffractograms of different (in shape and color) phyllosilicate grains (samples 8281, 8253, 82100) revealed that the d(060) region of the beige smectite grains from sample 82100 has a reflection with $d = 1.512$ Å, which corresponds to the parameter $b = 9.072$ Å. Hence, the smectite belongs to the Fe-bearing variety, i.e. nontronite.

In the light fractions (sample 8281, density <2.45 g/cm³; sample 670, <2.55 g/cm³) of mixed-layer minerals, which make up beige coprolites and varicolored (beige and pale green) grains, $b = 9.08$ Å. This value corresponds to the glauconite–nontronite composition of the mixed-layer minerals. Similar values of b (9.08–9.09 Å) are typical for illites (samples 8281 and 670) and micas proper (sample 670), indicating the glauconite composition.

In addition to the strong reflection in the d(060) region with $d = 1.513$ – 1.515 Å (Fig. 8), the mixed-layer minerals, illites, and micas (samples 8281 and 670) contain a weaker reflection with $d = 1.496$ – 1.499 Å ($b = 8.96$ – 8.99 Å). This observation suggests that the grains studied contain, in addition to glauconite minerals, a mechanical admixture of Al-mica or smectite. The latter case is related to grains with glauconite–nontronite minerals as the predominant phase.

The structural defect grade is very high not only in the mixed-layer glauconite–nontronite minerals but also in illites and micas of the glauconite composition. The powder diffractograms, for instance, are almost devoid of the reflections 112, $\bar{1}12$, 200, and $\bar{1}31$, the relationship between which makes it possible to assess the concentration of defects in the structure of glauconite minerals. Hence, one can assume that the structural imperfection of glauconite minerals is related to defects in the 2 : 1 layer packages, which are caused by the irregular 60°-fold sweeps of layers, rather than to the phenomena of the mixed-layer structure development (Drits *et al.*, 1993).

Hence, we can conclude that the varicolored authigenic minerals studied (samples 8281, 8253, 82100, and 670) make up a continuous structural-isomorphic series ranging from the smectite proper (nontronite) to the mixed-layer glauconite–nontronite minerals, the glauconite composition illites, and the glauconite proper. Similar X-ray analysis data were obtained by Lisitsina *et al.* (1976) for the 2:1 phyllosilicate samples collected near the Mexican coast.

CHEMICAL COMPOSITION

Based on the whole-rock microanalysis data, the three similar (in density and size) fractions of sample 670 are identical in chemical composition as well (Table 1). They are characterized by a high Fe₂O₃ content (20.12–20.38%) and a relatively low Al₂O₃ content (6.60–7.19%). The K₂O content is slightly higher in the heavy fraction, relative to the light fraction (6.81 and 6.10–6.19%, respectively).

The X-ray spectral microanalysis was performed with the application of a Camebax microprobe for some size and density fractions of glauconite grains (samples 670, 8281, 8253, and 82100), as well as the beige and pale green coprolites (samples 670 and 8281). In sample 670, the K₂O content increases from 5.04% in the light fraction to 7.78% in the heavy fraction (Table 1). In sample 8281, the respective values are 4.06 and 6.88%. The total Fe content, which sharply dominates over Al in samples, also somewhat increases in the same fashion in different fractions. The SiO₂ content, however, slightly decreases. The highest Al₂O₃ concentration (7.35%) is noted in beige coprolites characterized by a higher NaO (0.24%) and a lower K₂O content (4.06%). In sample 8281 grains, the pale margin (crust) was found to be similar to the central part, except for a lesser (by 1.3%) K₂O content.

Using the complete and incomplete whole-rock analyses and assuming that the anionic framework (O₁₀(OH)₂)^{–22} is constant, we calculated the crystallochemical formulas of minerals studied (Table 2). In general, the composition of the sample 670 minerals fits glauconite; however, the formula unit (f.u.) of glauconite from one sample (0.2–0.315 mm, 2.6–2.65 g/cm³) has a tetrahedral charge that is close to the upper limit of the charge in celadonites. As is well known, celadonites are characterized by a limited substitution of Si by Al³⁺ or Fe³⁺ (from 0 to 0.2 f.u.). The low substitution of Si by Al in tetrahedrons is also typical for the sample 8281 counterpart, in which the total Fe is higher than in sample 670. However, the comparison of data on these samples is tentative, because the microprobe data can differ from the whole-rock analysis data. For example, the microprobe analyses generally yield underestimated values of SiO₂ and Al₂O₃ but overestimated values of K₂O. As is evident from Table 1, precisely this situation is observed in the case of the sample 670 grains (0.4–0.63 mm, 2.65–2.7 g/cm³).

Table 1. Chemical composition of samples, wt %

Sample no.	Grain size, mm	Grain density, g/cm ³	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O ⁺	H ₂ O ⁻	Σ
670	0.63–0.315	2.2–2.45*	49.67	4.88	21.36		3.82	0.58	0.04	5.04	–	–	85.39
670	0.4–0.315	2.5–2.55	48.61	5.84	21.04		3.77	0.50	None	6.47	–	–	86.25
670	0.4–0.315	2.6–2.65	50.35	7.19	20.12	1.60	4.16	0.77	0.14	6.19	7.18	2.02	99.72
670	0.315–0.2	2.6–2.65	49.85	6.60	20.38	1.03	4.08	0.72	0.14	6.10	7.98	1.38	99.80
670	0.63–0.4	2.65–2.7	49.79	6.80	20.22	1.71	4.17	0.49	0.14	6.81	7.78	1.87	99.80
670	0.63–0.4	2.65–2.7	48.23	4.53	22.64		3.78	0.41	None	7.78	–	–	87.49
8281	0.63–0.2	2.3–2.4**	48.75	7.35	21.63		3.38	0.63	0.24	4.06	–	–	86.04
8281	0.63–0.2	2.35–2.45*	49.08	5.53	23.16		2.90	0.84	0.01	4.54	–	–	86.05
8281	0.63–0.2	2.45–2.6	50.59	4.53	24.06		3.55	0.36	0.01	6.88	–	–	90.00
8253	0.4–0.2		50.44	4.86	22.20		3.19	0.30	0.18	4.65	–	–	86.52
82100	0.4–0.2		48.27	4.79	23.01		3.18	0.87	None	5.00	–	–	85.32

Note: Samples 8253 and 82100 were not separated into density fractions. The water content was not determined in the Camebax microprobe analyses (G.V. Karpova, analyst).

* Pale green coprolites; (**) beige-colored coprolites.

Table 2. Crystallochemical formulas of samples

Cations			Tetrahedral		Octahedral				Interlayer		
sample no.	size, mm	density, g/cm ³	Si	Al	Al	Fe ³⁺	Fe ²⁺	Mg	K	Na	Ca
670	0.4–0.315	2.6–2.65	3.73	0.27	0.36	1.12	0.10	0.46	0.58	0.02	0.06
670	0.315–0.2	2.6–2.65	3.75	0.25	0.34	1.15	0.07	0.46	0.59	0.02	0.06
670	0.63–0.4	2.65–2.7	3.72	0.28	0.32	1.14	0.11	0.46	0.65	0.02	0.04
8281	0.63–0.2	2.45–2.6	3.81	0.19	0.17	1.36		0.41	0.64	0.01	0.05

DISCUSSION

The problem of the genesis of glauconite of any lithotype and age is controversial in the following aspects: the position of glauconite formation in the stadial process of lithogenesis, the source of primary material for the formation of glauconite grains, the mechanism of the formation (with respect to morphology and crystal chemistry), the role of biogenic factor in mineral formation, etc.

The corroboration of the authigenic nature of glauconite grains in present-day sediments is one of the most urgent problems. Let us scrutinize this problem on the basis of samples studied. Our experience in the investigation of glauconite-bearing sediments and the available numerous publications provide evidence that glauconite sediments often bear signs of mixing, roiling, and rewashing. These features may be related to a process of bioturbation or the variation in the basin's hydrodynamic activity during sedimentation. The sediments studied are not exceptions and indicate the existence of a mobile environment. With respect to the authigenic nature of certain grains, the interpretation of their

morphological features is ambiguous. Let us examine the facts in favor of glauconite formation *in situ*.

First, the varicolored glauconite and coprolite grains are much larger in size than the terrigenous matrix. This rules out the redeposition of grains from the older and unconsolidated sediments. During redeposition, grains of different rigidity and density could not be transported together and accumulated in great amounts in a single fine-grained sediment layer (for example, in sample 8281). Moreover, some grains are so extensively crosscut by cracks that their redeposition is impossible. The redeposition is also hardly possible when the glauconite grain margin is overgrown with a brittle radiolarian shell or diatom frustule.

The irregular, often clastic form of glauconite grains was formed mostly owing to the breakup of fractured varieties during the multiple sediment mixing by fossorials. Local washouts of sediment is likely a secondary factor. The simultaneously developed coprolites of fine-grained material, which are analogous to the host matrix, could also breakup. The presence of pale-colored rims and zones on the surface of dark green grains of glauconites and their fragments, as well as on the surface of glauconitized (to a variable extent) coprolites, suggests that the alteration

process continued in the sediment. This inference is also supported by the fact that the exterior pale-colored zone penetrates and mimics the contours of wide fractures.

Microglobules in coprolites demonstrate a close paragenetic relationship with the remains of diatoms and radiolarians. This is a convincing argument in favor of the active involvement of microorganisms in the formation of authigenic clay minerals. The primary gel nature of glauconite is no longer doubted (Drits and Kossovskaya, 1991). The Fe–Si gel was likely formed in places that were favorable for the activity of bacteria and the consequent decomposition of the polymineral microgranular terrigenous material. In the samples studied, such places are represented by coprolites and microsectors that were enriched in organic matter and subsequently segregated as irregular grains. As was mentioned above, the cellular nanostructure of the authigenic clayey material is widespread in beige to pale green coprolites and irregular grains. It is highly probable that this nanostructure is a result of colloid particle crystallization (Figs. 6a–6d). The morphology and dimension of microglobules, which are common in the nanostructure, are indicative of the fossilized bacterial colonies.

Bacterial coccus is very rapidly formed, as is evidenced by the growth rate of microcolony *Arthrobacter pyridinolis*. During the experimental cultivation of bacteria on an agar slide, the transverse size of coccus attained more than 30 μm in 22 h (Schlegel, 1985, Fig. 3.2). The fast development of coccus could be responsible for its partial fossilization prior to the silicate gel crystallization and cellular structure formation. Cryptocrystalline sectors of silicate gel retain fossilized remains resembling irregular bacillus clusters (Figs. 7e, 7f).

Based on the above-described facts, we can argue that the green grains of the glauconite–nontronite series minerals were formed *in situ* in sediment that was constantly reworked by fossorial organisms, i.e., under the conditions of an active involvement of microorganisms. Several researchers have emphasized that glauconite is formed in sediments with abundant organic matter, naturally implying the participation of microorganisms that decompose the organic matter. The recently published work of Vernadsky (1983) has revealed that this prominent scientist had confidently suggested the glauconite formation with the participation of microorganisms as far back as 70 years ago. Recently, Gorshkov *et al.*, (1992a, 1992b) reported distinct evidences of the bacterial activity. They observed nontronite in replacement products of the Si-bearing bacterial particles of protoferrihydrite detected in various oceanic hydrothermal edifices. Later, evidence for the presence of fossilized bacterial remains in glauconite nuclei of Chancelloriidae from Lower–Middle Cambrian rocks of the northern Verkhoyansk region was reported in (Geptner *et al.*, 1994). Additionally, the biogenic origin

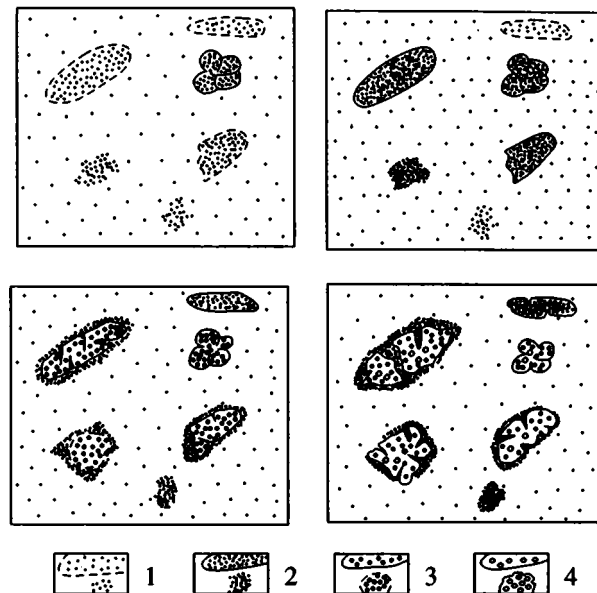


Fig. 9. Schematic stages of the evolution of the glauconite–nontronite series grains. (1) Pale brown; (2) beige; (3) pale green; and (4) green.

of nontronites has been ascertained for the submarine hydrothermal rocks of white smokers (Kohler *et al.*, 1994).

Based on the available data, we can suppose that the formation of glauconite grains in sediment was not interrupted until the sampling moment; i.e., the grains were continuously growing at different rates in different sectors of the sediment. The evolution of green grains can be divided into three distinct stages: (1) grain formation; (2) grain breakup during bioturbation; and (3) the formation of pale rims and zones on the fragment surface. These stages may not coincide in different grains. Therefore, coprolites can occur together with grains having various mineralogical features. The evolution of authigenic grains of the glauconite–nontronite series can be divided into the following phases (Fig. 9).

(1) At the first phase of authigenic clay mineral formation, the pale brown sediment undergoes intense bioturbation, mixing, and possible slight rewashing. It contains abundant coprolites that do not differ in color from the host matrix. As a result of bioturbation and rewashing, a part of coprolites is disintegrated and gets into the sediment as fragments. The organic matter is irregularly distributed. It is abundant in coprolites, fine-grained material within foraminiferal shells, and some sectors of sediment with diatoms and radiolarians. The clayey component consists of Al-smectite along with minor illite and chlorite.

(2) Under an active influence of the microbial activity in coprolites, the fine-grained material is transformed in the interior zone of foraminiferal shells and some sectors of the sediment. Consequently, the Fe–Si gel is crystallized and the nanostructure is developed.

The altered sectors of matrix and coprolites become beige-colored. Some sectors of the altered sediment acquire a pale green color and compact nanostructure. Beige-colored aggregates (density 2.3–2.4 g/cm³) in the authigenic clayey material incorporate the mixed-layer glauconite–nontronite minerals with a predominant smectite component. Illite and chlorite are the subordinate minerals.

(3) As a result of the continuing influence of bacteria upon terrigenous material transformation, beige-colored grains and coprolites acquire a pale green color, and some aggregations are expanded. Open cracks are developed on the surface of some coprolites, leading to the origination of the specific brain-shaped structure that is commonly considered an evidence for gel dehydration (Chukhrov, 1955). Odin attributes this phenomenon to the swelling of grains during their glauconitization. In some cases, the transformation of the fine-grained material continues along the periphery of grains and coprolites as well, resulting in the bleaching of the sedimentary terrigenous material along the margins of grains and the crack network. In pale green grains and coprolites, the content of swelling layers in the glauconite–nontronite mineral structure drops to 25–50%, the K₂O content rises to 4.5–6.5%, and the chlorite admixture disappears.

(4) Under favorable conditions, the terrigenous material transformation continues in certain coprolites, grains, and their fragments formed by sediment mixing. The grains have a green color. Pale-colored rims are developed around green grains, coprolites, and their fragments. The interior zone of grains is characterized by the development of nanostructure, as well as a compact structure (with a random distribution of flakes) resembling the nanostructure of glauconite grains. In places where the bacterial activity is particularly high, the grain size is increased as a result of the growth of rims and the possible intense formation of authigenic clayey minerals inside grains. The compositions of clayey minerals fit the micaceous and hydromicaceous varieties of glauconite with the K₂O content within the range of 6.10–7.78%.

The above-described observations indicate that the glauconitization rate of sediments depends on the depth level. It is maximum in sediments with large (0.4–1.0 mm) green grains of illite (sample 8281) and glauconite (sample 670). In the sample 82100 sediments, the majority of grains are represented by pale-colored nontronite, while the fine (0.2–0.4 mm) green grains of the mixed-layer glauconite–nontronite composition are scarce. This can suggest either unfavorable conditions for glauconite formation or an immature stage of glauconitization in the specific sector of seafloor. In the sample 8253 sediment, the glauconitization is characterized by a moderate intensity, and the content of grains, represented by the glauconite–nontronite series minerals of the finer (0.2–0.4 mm) fraction, is reduced, relative to the sample 8281 sediment.

CONCLUSION

(1) In the present-day Pacific sediments located at different depths and in various structural–geomorphological settings, glauconite grains are formed *in situ* with an active involvement of microorganisms.

(2) The biochemogenic origin of glauconite grains from the present-day Pacific sediments is definitely revealed by the examination of their nanostructure. The cellular nanostructure of the authigenic clayey material, formed as a result of the silicate gel crystallization, is registered at the earliest stages of the development of nontronite and glauconite–nontronite grains. Based on shape and size, coccoid segregations, often included in the cellular structure, can be considered the fossilized bacterial colonies. Cryptocrystalline sectors incorporate the bacillus-type nanostructure that can also be identified as fossilized bacteria. Such structures were first discovered by the authors in nuclea of the nontronitic Chancelloriidae from Lower–Middle Cambrian rocks of the northern Verkhoyansk region.

(3) Glauconite grains are formed in bioturbated sediments that are enriched in organic matter, such as coprolites, foraminiferal shell nuclea, or matrix with remains of diatoms and radiolarians.

(4) The process of glauconitization is registered by the alteration of several mineralogical features (color, microstructure, nanostructure, X-ray characteristics, mineral composition, chemical composition, etc.) of both the primary material (terrigenous Al-smectite) and the subsequent phases ranging from Fe-smectite (nontronite) or glauconite–nontronite to illites and glauconite micas.

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New Data on the Structure of the Upper Danube Deep-Sea Fan

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Abstract—The morphology, structure of Quaternary deposits, and processes of Late Quaternary sedimentation within the boundaries of a poorly studied and intricate area of the Danube deep-sea fan at a site 15 × 15 km in size have been comprehensively studied using a complex of methods (high-resolution continuous seismoacoustic profiling, echo sounding, and study of sediments). Four complexes of deposits, three of which were formed during the Würmian and Riss times, have been described. Specific characteristics of the sedimentation process during the active and passive phases of fan formation have been studied on the basis of results obtained from analyzing sections of Late Quaternary sediments.

INTRODUCTION

The Danube deep-sea fan is a large accumulative body, located in the western part of the Black Sea and expressed in the bottom relief in the form of NW–SE-oriented uplift.

Specific features of its structure and morphology, as well as the composition and dating of its sediments are reflected in few publications (Kazantsev and Shainurov, 1978; Konyukhov *et al.*, 1988; Konyukhov and Ivanov, 1989; Starovoitov *et al.*, 1990). At least four generations of fans formed during the Quaternary time were established, and specific features of the sections of Late Quaternary sediments were studied in these bodies.

The purpose of this work is to study in detail the northeastern part of the fan within the boundaries of a small site 15 × 15 km² in size, located in the area of an especially complicated structure at an abrupt turn at the main valley (Fig. 1). The complex of methods included the echo sounding of the bottom, high-resolution continuous seismoacoustic profiling (CSAP), which was for the first time applied to this region, as well as the study of sediments taken by the gravity corer. Altogether, twenty-three CSAP profiles and echo-sounding measurements were accomplished along the grid at a 1–1.5 km interval, fifteen cores of Late Quaternary sediments were taken from four profiles, intersecting various sites across the strike of the fan valley.

Excitation of elastic waves during the seismoacoustic investigations was carried out using an electric-spark source with the total energy 2 kJ, realized through fifty electrodes, which ensured the record resolution along the vertical equal to 3–4 m. Despite such limited power from the source, atypical for deep-water works, reflecting boundaries lying down to 800 m beneath the bottom (at a water depth of 1500–1800 m) were successfully and reliably traced. Substantial depths at a relatively high resolution may be evidently explained by

extremely favorable seismogeological conditions of the fan.

THE FAN MORPHOLOGY

As is seen from (Figs. 1a, 1b), the area under investigation encompassing the middle and distal parts of the fan (sea depths from 1400 to 1800 m). In the bottom relief, the fan represents a NW–SE-extended uplift with an amplitude up to 500 m and width up to 10–15 km. A central valley, framed with thick alluvial levees, is extended along the axis of this accumulative edifice. The depth of its downcutting attains in some places 400–500 m, and its width in the upper part is 2–3 km. At sea depth of about 1600 m the valley deflects toward the northeast and abruptly changes its strike for a sub-latitudinal one. Within 20–25 km the bottom relief becomes undistinguishable.

The transverse profile of the channel in the northern part of the region under study is substantially different from the southern one. In the north, there is a typical V-shaped downcutting with a clearly pronounced thalweg. Its depth, with respect to the alluvial levees, attains 450 m, and there are terraces in some places on the southwestern slope. In the south, the cross section becomes U-shaped, the depth of the downcutting diminishes by half, and the thalweg is filled with a young sedimentary sequence 30–40 m thick.

The profile transformation and the valley bottom flattening, according to the echo sounding and CSAP data, become distinctly pronounced from sea depths of about 1500–1550 m immediately behind the fan's intricate site, where the valley turns northeastward almost at a right angle. The morphology of this site and its change with increasing distance from the turning point is clearly seen on the pioneer detailed bathymetric map (Fig. 1c). At first, the downcutting is 35–40 m deep and 1 km wide. The valley then rapidly deepens and widens. Its transverse profile is asymmetrical. A thick

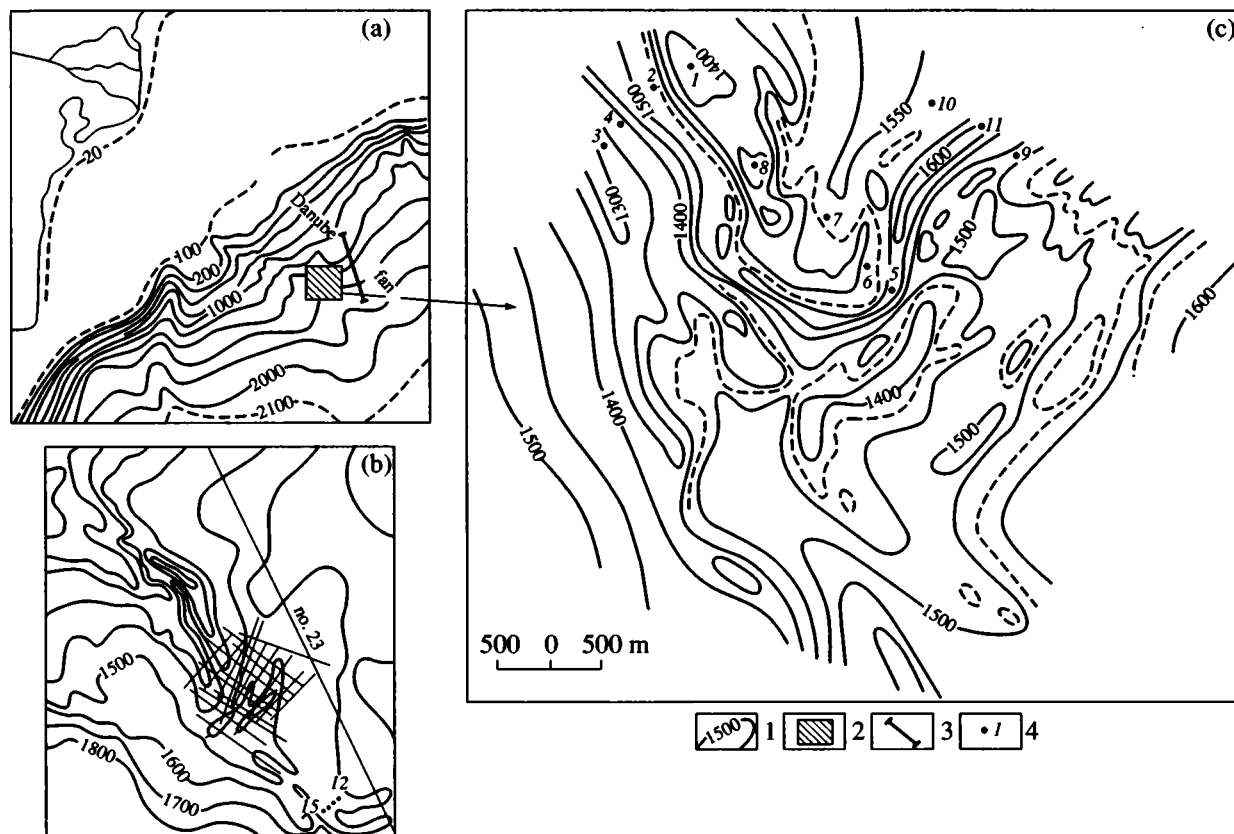


Fig. 1. Region under investigation (a, b) and bathymetric chart (c). (1) Isobaths (m); (2) investigated site; (3) echo-sounding and seismoacoustic profiles; (4) sampling points of sediments.

alluvial levee with the width exceeding 2 km and height attaining 200 m is formed on the right side. The left-hand alluvial levee thickness is approximately half as much. It is substantially narrower, and its surface is more complicated. Further northeastward, the down-cutting diminishes, the cross section becomes more symmetrical, and the V-shaped configuration is preserved.

THE FAN STRUCTURE (BASED ON CSAP DATA)

Seismoacoustic profile 23, intersecting a large ravine in the northwestern part of the area under investigation and two branches of the valley (Fig. 1), provides the most comprehensive notion of the fan structure. The profile is located along the northeastern slope of the main fan and intersects the system's different-age generations across the strike (Fig. 2). From the seismic record features we distinguished four sedimentary (seismostratigraphic) complexes, the first three of which belong to the fan itself.

The largest complex (Fig. 2, 1) occupies the southern one-third of the profile and represents a peripheral segment fan of the central valley. The thickness of sedimentary sequence in its axial part constitutes about

600 m, and the width is more than 25 km. The complex is restricted from the bottom by an intense low-frequency reflecting horizon (RH-1), which can be traced with confidence along the whole length of this profile and all other studied profiles. A characteristic feature of horizon RH-1 is its essentially even relief and regional southward inclination (possibly representing a surface of the leveled continental slope). Despite the fact that horizon RH-1 serves as an acoustic basement, fragments of the underlying reflections give grounds to suppose that it locates the surface of angular discordance and possibly separates an earlier generation of the Danube fan (Starovoitov *et al.*, 1990).

The internal structure of the complex on the time section is chiefly represented by very weak and long reflecting horizons, and acoustically transparent sediments. Some sites with sufficiently intense short and sophisticated reflections evidently mark buried channels. Here, fine-grained turbidites may be replaced by the coarser varieties.

The central valley, pronounced in the present-day bottom relief, is, as previously mentioned, filled partially with sediments and has a U-shaped profile. Against the background of weak reflections, an intense reflecting horizon (RH-2), evidently corresponding to a change in sedimentation conditions (a transition to the

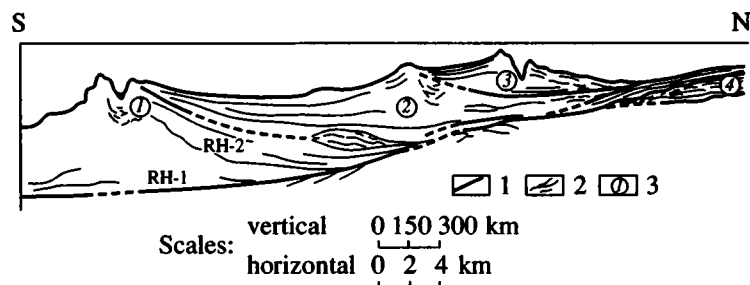


Fig. 2. Seismogeological section along profile 23 (see Fig. 1). (1) Boundaries of seismostratigraphic complexes; (2) reflecting boundaries; (3) seismostratigraphic complexes; RH-1 and RH-2 are reflecting horizons 1 and 2.

normal pelagic process), is extended inside the complex. It seems that at this site we have an example of inherited formation of the main fan with a stable position of its multistage valley. A wedging-out of separate internal subdivisions of the first complex, according to the scheme of basal adjoining, is observed at a distance of about 15–20 km northward of the axial valley. At the same site, a large lens with chaotic and “undulating” reflections is located, which, in our opinion, may correspond to a slide block.

The axial part of the second generation fan (complex 2) with a buried valley and high southern near-channel levee, expressed in the bottom relief as a small uplift, immediately overlies the wedging-out zone of the complex 1. The maximum thickness of complex 2 attains 300 m. The intense reflecting horizon at its base is clearly seen in the central and northern parts of the profile. Southward of the valley, the amplitude of this reflection rapidly diminishes, and the boundary between complexes 1 and 2 can be drawn here only arbitrarily. In this interfluvial area, expressed by extended, weak, smooth reflecting horizons, the fine-grained turbidites were likely accumulated as a result of tidal action over the near-channel levees. The northern half of complex 2 is represented by intermittent, hummocky, and in some places chaotic reflections, which point to a more dynamic sedimentation environments.

The second generation fan is discordantly overlapped by the youngest sedimentary complex 3 distinctly pronounced in the relief by a symmetrical suprafan with a V-shaped central valley, the morphology of which was discussed above. In the central part, the third generation fan is 200 m thick and 20 km wide, and the downcutting is approximately 100 m. The right-hand side of the suprafan, as well as that of the underlying body, is characterized by smoothly extended, reflecting horizons, while the left-hand (northern) side reveals less regular intermittent reflections with a large number of diffracted waves formed on the uneven surface of the bottom.

Sedimentary complex 4 is situated in the northern part of the profile and characterizes a continental slope adjoining the fan on the north. It makes up a lenticular body more than 25 km long, wedging out in a southern

direction towards the suprafan. The maximum thickness of the complex is 100 m. Its structure is represented by very weak, extended reflections in the northern part and by short, uneven, and in some places chaotic, reflections in the southern part. The body is overlain by a 50-m-thick member of well-stratified sediments, distinguished by much more intense low-frequency reflecting horizons. The 10–30-m-thick series of sediments, expressed by intense medium-range reflections, occurs at the base of the complex. These sediments fill irregularities in the top of the underlying, acoustically transparent sequence.

In our opinion, the young wedge-shaped body was formed by turbidity flows, running from the northwest down a low-angle, and wide ravine. Its formation was evidently indirectly connected with the Danube canyon activity. The lower part of the complex (the infilling sediment facies) is composed of sediments brought by high-density flows. Judging from the character of seismic record, the entire southern half of the body up to its wedging-out zone represents a creep apron. The intense reflecting horizon at the top of complex 4 most probably corresponds to horizon RH-1, i.e., to the base of the first generation fan. Hence, complex 4 is the oldest one. Note that the thickness of sediments above horizon RH-1 grows from 30 m in the northwest to 600 m in the southeast, to illustrating the abrupt increase of sedimentation rates within the canyon–fan system with respect to adjacent areas.

SPECIFIC FEATURES OF SEDIMENTS

The structure and composition of Late Quaternary sediments crowning the deep-sea fan section, as well as general features of the sedimentary process, have been studied on the basis of analysis of fifteen cores taken in different facial zones (Figs. 1, 3). The normal deep-water Late Quaternary section in the western Black Sea can be divided into three stratigraphic horizons: Recent Black Sea, Old Black Sea, and Neoeuxinian (Arkhangel'sky and Strakhov, 1938; Kuprin *et al.*, 1984).

The Recent Black Sea horizon consists of a rhythmic alternation of: (1) OM-enriched bands, (2) clayey bands, and (3) coccolitic bands. The thickness of each band is up to 1 mm. The total thickness of the horizon

does not exceed 30–40 cm. The Old Black Sea horizon, about 40 cm thick, is composed of laminated sapropel with frequent interlayers of aragonite silt in its lower part. The Neoeuxinian horizon is composed of clayey mud. Interlayers of calcareous silt and diatomaceous ooze are contained in its upper part, while its lower part comprises clots and interlayers of hydrotrillite silt.

All the above-mentioned horizons can be distinguished in the studied cores. A sharp difference in the structure of Recent Black Sea and Old Black Sea sediments, on the one hand, and Neoeuxinian sediments, on the other, is noted, which reflects changes in their formation mechanism.

In the majority of cores taken from different parts of valley channels, their slopes, and tops of near-channel levees, Recent Black Sea and Old Black Sea sediments are represented by normally precipitated laminated varieties, i.e., by clay-coccolith and sapropel muds, which are almost completely free of the detrital admixture. Disturbances in stratification, caused by creep processes, are observed in sapropel only at Section 2 (Fig. 3) in the axial part of the valley. In addition, the middle part of the sapropel horizon has a lumpy structure, which may be connected with redeposition. The total thickness of the horizons varies between 23–58 cm. The accumulation rates of the Recent Black Sea and Old Black Sea sediments constitute 3–9 and 3–10 cm ka⁻¹, respectively.

A different type of sediments was exposed in the near-axial part of the valley branch at stations 5 and 11 (Fig. 3). The Site 5 section is as follows (from top to bottom): (1) layer of laminated clay-coccolith ooze with a 1-cm-thick diatomite band (11 cm); (2) discordantly underlying layer of greenish gray, loose, lumpy diatomaceous clay ooze with small coccolith clots (at about 30 cm); (3) interlayer of coccolith ooze (3 mm); (4) layer of more dense, greenish diatomaceous clay mud with coccolith clots (containing diverse diatom shells and their numerous detritus along with the fragmental terrigenous admixture); (5) layer of laminated coccolith ooze (11 cm); (6) horizon of pure coarse-banded diatomite (18 cm) with intercalation of up to 1.5-cm-thick foliated (cardboard-like) and denser homogeneous green mud interlayers (distinctly displaced in one area) and one dark blue interlayer.

The lower 112–145 cm interval consists of four units (thickness 17, 5, 6, and 5 cm, respectively) that can be subdivided into lower part (sapropel-like mud with sapropel pebble), middle part (finer clay mud with dissemination of sapropel and coccoliths), and upper part (pure coccolith ooze) with one 1-mm-thick silt band at the level of 129 cm. Dark green sapropel mud (with interlayers of diatomites and thin bands of silt in the lowest part) constitutes the base of the core. Remains of diatoms and clastic material are dispersed within the sapropel mud.

A similar section was exposed at Station 11 (Fig. 1), situated downstream of the valley. The increase of

thicknesses in the diatomaceous clay horizons and the decrease of thicknesses in the coccolith silt and diatomite are its characteristic features.

The structure of Neoeuxinian sediments differs substantially from those described for the Recent Black Sea and Old Black Sea horizons owing to different conditions of sedimentation during the Late Pleistocene. This difference manifests itself, on the one hand, in the universal presence of fine-grained turbidites, represented by fine-sand, coarse-silt, and clay varieties, and, on the other hand, in the incompleteness of sections due to the omission of separate horizons. In particular, the latter circumstance is displayed through the nonuniversal distribution of diatomaceous oozes, the different thicknesses of calcareous muds, and sediments above hydrotrillite mud, etc.

Sometimes, a substantial part of Neoeuxinian horizon is represented by rhythmical interlayering of relatively pure clay muds and coarser-grained silt muds and clayey-silt muds (less commonly, coarse silt and fine sand). Clay muds, which represent normally precipitated pelagic sediments vary in thickness from several centimeters to a few tens of centimeters. They contain a small amount of silt uniformly dispersed within the mud mass.

Deposits of turbidity flows are expressed in two varieties similar to the lithotypes of the upper elements constituting the Bouma cycle. Foremost, these are discrete interlayers of silt and, more seldom, fine sand with a small admixture of clay material. The thickness of interlayers varies from several millimeters to 1 cm. Contact with host muds are distinctly visible. A thin horizontal, undulating-lenticular, and sometimes vaguely pronounced oblique bedding is often inherent in thicker varieties.

However, layered sediments with the gradational structure prevail in the majority of cores. Poorly sorted silt muds with a considerable admixture of clay material lie in the lower part of each layer. They grade upward into predominantly clay mud enriched in sandy silt material. Among the latter, diversely rounded quartz, muscovite, fragments of carbonate rocks, and plant detritus prevail. The thickness of separate layers varies from a few millimeters to 10–15 mm. In a number of cases, they determine the rhythmical structure of Neoeuxinian deposits. Thus, in cores from Station 15, 35 of such layers can be counted in the 56–104 cm interval and 80 of them in the 150–195 cm interval. In other sections, the occurrence frequency of these layers diminishes.

Another specific feature of the Neoeuxinian sediments is the presence of creep structures in the form of flow folds and intrusion of alien substances with the admixture of coarse-grained material. Such features are chiefly observed on the internal sides of the fan valleys.

Analysis of the studied Late Quaternary sediments showed that, except for thin (less than 1 m) Holocene and late Neoeuxinian normal pelagic muds, the remain-

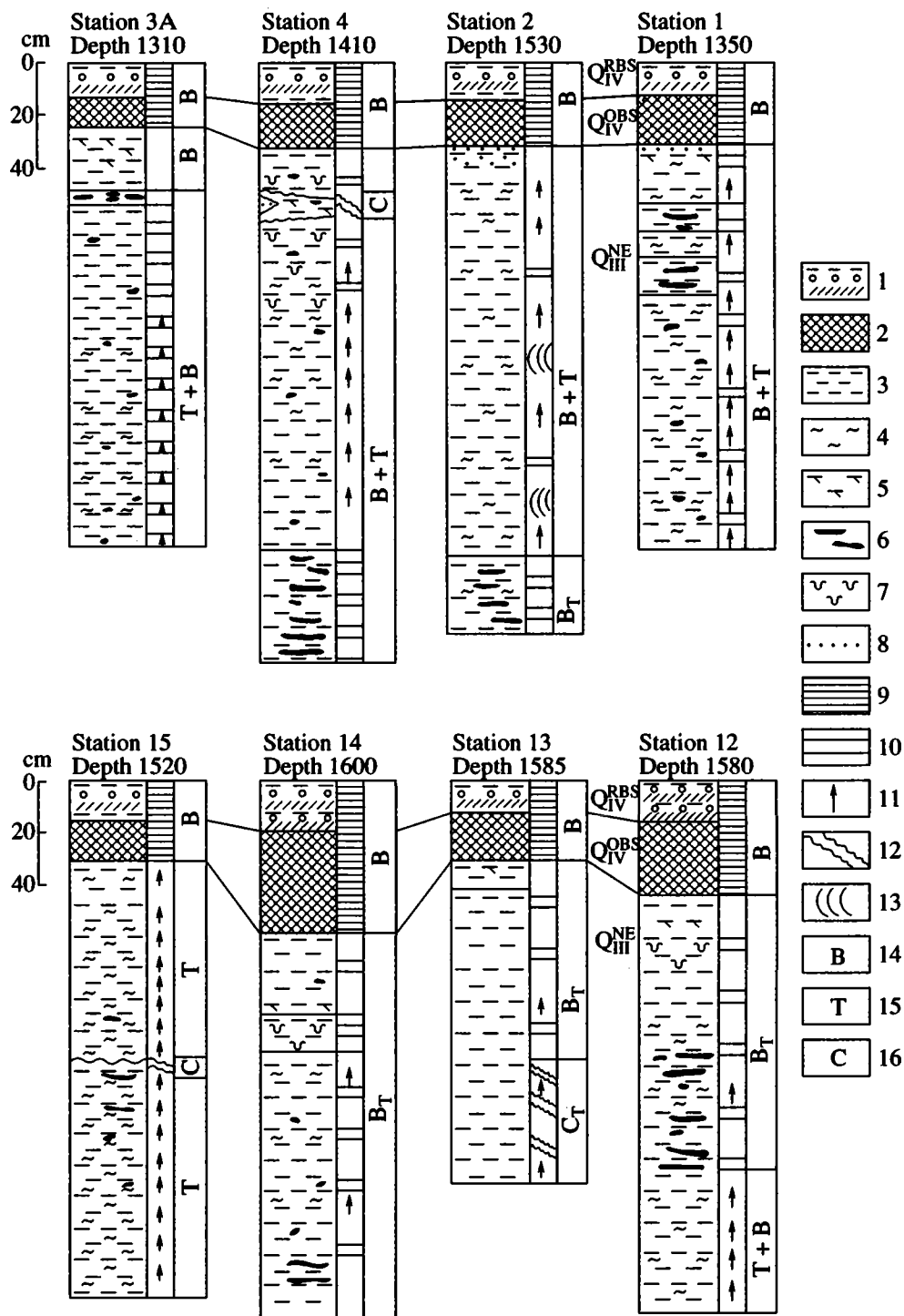


Fig. 3. Sections of Late Quaternary sediments. Lithotypes of sediments: (1) clay-sapropel-coccolith mud, (2) sapropel, (3) clay mud, (4) silt, (5) calcareous mud, (6) hydrotroilite, (7) diatomaceous ooze, (8) sand; structures: (9) microlaminated, (10) banded, (11) gradational, (12) slid, (13) cross-bedded. Genetic types of sediments: (14) background (B), (15) turbidites (T), (16) creep (C). Age of sediments: (Q_{IV}^{RBS}) Recent Black Sea, (Q_{IV}^{OBS}) Old Black Sea, (Q_{III}^{NE}) Neoeuxinian.

ing part of the sections of Late-Pleistocene sediments in the fan is represented by deposits of turbid flow sediments, the occurrence frequency and thickness of which differ in different zones.

DISCUSSION

The age correlation of the distinguished fan generations is problematic due to the absence of deep-sea boreholes, preventing the accurate stratigraphic division of the studied sequence of sediments. Therefore, the only method to solve this problem is the assessment of thickness and accumulation rate for Late Quaternary sediments and extrapolation of these data to the whole exposed section. Several variants of calculations may be carried out if we take into account the observation that for the large deep-sea fans of Amazon and Nile, the average accumulation rates of sediments, represented chiefly by turbidites, constitute less than 115 cm ka^{-1} and at least 100 cm ka^{-1} , respectively (Damuth and Kumar, 1976; Maldonado and Stanley, 1979).

The maximum thickness of deposits on the right-hand alluvial levee, belonging to the third (youngest) generation of the Danube fan attains 200 m. Suppose then that this fan was formed during the last glacial stage (late Würmian, 25–10 ka ago), when the Black Sea level lowered down to –80 or –100 m. The time of accumulation of pelagic late Neoeuxinian (calcareous, diatomaceous, and clayey) and Holocene (sapropel and coccolith) muds can be assessed as 9 ka (from the beginning of restoration of the bilateral connection between the Black and Mediterranean seas at a level of –30 m). In this case, their total thickness (1–1.5 m) is virtually not reflected on seismotapes, as it lies beyond the resolution limits of the methods applied. Consequently, the suprafan, composed of sediments brought by turbid flows, was formed during the period constituting about 16 ka. The average sedimentation rate will be $500\text{--}800 \text{ cm ka}^{-1}$ over 25 ka and $800\text{--}1300 \text{ cm ka}^{-1}$ (or $8\text{--}13 \text{ mm yr}^{-1}$) over 16 ka. This rate is by about an order of magnitude higher than on the fans of the Amazon and Nile.

Let us assume that the suprafan was formed during the entire Late Pleistocene (Würmian) time in the period between 70 to 10 ka ago. In this case, the average sedimentation rates would constitute $150\text{--}250 \text{ cm ka}^{-1}$ or $1.5\text{--}2.5 \text{ mm yr}^{-1}$, while accumulation rates of turbidites would constitute $2.5\text{--}4 \text{ mm yr}^{-1}$ (minus the time of Holocene and Middle Würmian, when pelagic sediments were deposited). The last figures, although they exceed the rates typical for other fans, seem to be closer to the real ones, although the turbidite units described above, were formed annually.

Taking into account the calculations accomplished, we think that the suprafan and its seismostratigraphic complex 3 were formed during the Late Pleistocene (Würmian) and Holocene time. As thus, the turn of the central fan valley to the north-east took place in the pre-

Würmian time or at the beginning of the Würmian time. This evidently occurred as a result of the channel blocking due to the collapse of its sides, as suggested by specific features of the bottom relief, clearly seen on the bathymetric chart.

The maximum thickness of the second sedimentary complex 2, as previously noted, is 300 m. Based on the average rate of its accumulation equal to 2 mm yr^{-1} , its formation time constitutes 150 ka. With the duration of the Riss–Würmian interglacial period equivalent to 30 ka and with the rate of accumulation of pelagic Karangian (Riss–Würmian) muds equal to 10 cm ka^{-1} (analogous to that of Holocene interglacial muds), their thickness will amount to several meters. Precisely this type of horizon (with a thickness and seismic record typical for normally layered sequences) separates complexes 2 and 3. Consequently, judging from the calculated duration (from 250 ka to 100 ka ago), complex 2 was accumulated during the Riss glacial epoch and corresponds to Paleoeuxinian layers.

If horizon RH-1 is an isochronous surface, whose age, according to our calculations, is 250 ka, then the average accumulation rate of sedimentary complex 1 will be about 2.5 mm yr^{-1} , i.e., confined within the same limits as the above specified accumulation rates of complexes 2 and 3 of the fan. Therefore, this complex 2 is actually a stable (in time and space) part formed parallel to other complexes.

Based on the material presented, it is possible to note the migration of younger lobes (complexes 1 and 2) of the fan in the northwestern direction with simultaneous disappearance of the oldest lobe composed of sedimentary complex 1.

Finally, if the formation time of the normally layered member of sediments above the seismoacoustic complex 4, overlying RH-1, constitutes 250 ka, then the accumulation rates of evidently pelagic muds on the continental slope northward of the fan will turn out equal to $20\text{--}25 \text{ cm ka}^{-1}$. Complex 4, judging from its internal structure, represents sediments of a turbidapron, and was formed during the pre-Riss time, in several stages.

CONCLUSION

The complex geological and geophysical work accomplished has made it possible to comprehensively study the structure of the upper part of the Danube deep-sea fan.

(1) The high-resolution CSAP, data has made it possible to identify three generations of the fan and to reveal their internal structure and interrelations. The lower boundary of the complexes is isochronous and represents the pre-Riss surface of leveling. The fan generations were intensely formed during the Riss and Würmian glaciation epochs, when deep regressions of the Black Sea took place. In these circumstances, the eastern part of the fan grew steadily throughout the

entire time it was studied, while the other two generations are connected with the migration of waterway channels and were formed during the Riss and Würmian time.

(2) The study of Late Quaternary sections in the fan showed that normally precipitated muds are sharply subordinate, while the major part is represented by terrigenous fine-grained turbidites, distributed in all facial zones. It is possible to argue that the fan generations established are composed of analogous formations.

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Polycrystalline Diamond from the Udachnaya Pipe, Yakutia: Mineralogical, Geochemical, and Genetic Characteristics

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Abstract—The aggregate consisting of three diamond varieties (bort, carbonado, and yakutite) reveals an extremely complicated structure with various syngenetic inclusions of native metals, oxides, sulfides, and chlorides. The REE pattern is typical of that for kimberlites. Elevated contents of elements characteristic both for mantle and crustal environments were established. Polycrystalline diamonds are supposed to be formed from an oversaturated substantially gaseous phase under conditions of extreme thermodynamic disequilibrium owing to drastic temperature and pressure differences, which are typical of decompression environments in shallow-seated explosion structures. The specific features of the mineral composition of inclusions and the distribution of REE and other elements are proposed as criteria for the genetic relation of placer polycrystalline diamonds to their provenances.

Although researches have carried out numerous long-standing studies of natural objects, and experimental works, the majority of researchers share the opinion on the mantle-related formation of diamonds, yet their origin remains a very complicated and debated problem. The genesis of polycrystalline diamonds (carbonado and yakutite), which were commonly investigated using samples from placers, is most controversial. Various hypotheses, including very exotic ones, have been proposed: the impact metamorphism, the effect of radiation, etc. (Kaminskii *et al.*, 1985; Kaminskii, 1987; Shibata *et al.*, 1993).

This paper is based on results of a comprehensive study of a polycrystalline diamond sample from the kimberlite located in upper part of the Udachnaya pipe, where such diamonds are rather abundant (Zinchuk *et al.*, 1993). The sample represents a complex aggregate consisting of diamond monocrystals and a polycrystalline cement which fits both the carbonado and yakutite in structure. The results obtained are of principal importance since such diamonds might be a source of placers with a noticeable amounts of carbonado and yakutite as a result of the erosion of upper parts of diamond-bearing pipes like Udachnaya pipe and the partial disintegration of diamond aggregates.

GEOLOGICAL SETTING

The polycrystalline diamond sample was taken at the initial stage of the Udachnaya pipe mining (1975–1976) in the Daldyn–Alakit district of the Yakutian province. The diamond was taken from the kimberlite at a depth of a few tens of meters from the surface. As

of yet, this pipe is among the most well-known, as the results of its investigation were reported in numerous papers and monographs.

According to the data for an exploration and mining down to a depth of 1200 m, the Udachnaya pipe is characterized by a complicated geology and is composed of western and eastern pipelike bodies that merge at a depth of about 250 m and form a distorted octuple figure (Zinchuk *et al.*, 1993). The diamond-bearing diatreme intrudes a thick pile of Lower Ordovician and Upper–Middle Cambrian sedimentary rocks (dolomite, limestone, argillite, siltstone, sandstone, and conglomerate), which are severely altered and dislocated along the faults. The displacement of beds of country rocks from the contacts is as much as 200–250 m.

The Udachnaya pipe reveals 3–4 autonomous phases of the kimberlite melt injection (Ilupin *et al.*, 1978; Zinchuk *et al.*, 1993). Its upper part (down to 200 m from the surface) mainly consists of olivine kimberlite breccia, which is severely serpentinized and carbonatized. Abundant xenoliths of carbonate rocks (10–30 vol %) occasionally attain a few tens of meters in diameter. Mantle-derived xenoliths, i.e. serpentinized dunite, garnet lherzolite, garnet harzburgite, spinel lherzolite, and eclogite, are permanently encountered and occupy 0.1–0.6 vol % (Zinchuk *et al.*, 1993).

The spatial distributions between various morphological types of diamond deduced from the mining survey data are principally important. Diamonds were extracted from samples by a chemical decomposition. Studies at three levels (25, 115, and 190 m from the surface) of the western and eastern bodies have shown that

the main morphological groups of diamonds remain virtually identical everywhere. Differences in the abundance of inclusions, the surface structure, defects, color, etc., are also negligible (Zinchuk *et al.*, 1993).

Significant differences were pointed out only for the morphological group, which includes diamond aggregates and intergrowths (i.e., the polycrystalline varieties). Their average amount decreases from 28% (occasionally up to 60%) at the upper level (25 m) to 21% at the level of 115 m and 9% at the lower level (190 m) (Zinchuk *et al.*, 1993). Hence, the polycrystalline diamond is widespread in the near-surface part of the Udachnaya pipe, where it accounts for not less than a quarter of the total volume of morphological groups. Its amount sharply diminishes with depth, especially in the interval between 115 and 190 m.

In this situation, it is worthy to note that the Udachnaya pipe is most likely eroded only for a few hundred of meters. In particular, it is supported by a finding of xenoliths of fossiliferous Llandoveryan carbonate rock at a depth of about 800 m. During the emplacement, this rock was located above the present-day surface and was then moved down to 1000 m (Ilupin and Kryuchkov, 1975).

During the study of diamond-bearing eclogite and peridotite xenoliths from the Udachnaya pipe, all morphological varieties of diamond were characterized except for a group of aggregative diamonds (Ponomarenko *et al.*, 1976, 1980; Zinchuk *et al.*, 1993). It should be noted that the polycrystalline diamond has never been detected in diamond-bearing xenoliths from other pipes (Sobolev, 1974).

Thus, the mode of polycrystalline diamond occurrence in the Udachnaya pipe, i.e. its extensive development in the upper part of the pipe and the sharp decrease in depth, in combination with the lack of such a diamond in diverse xenoliths indicates that it was most likely formed in the near-surface zones of diatremes during the emplacement of the first portion of kimberlitic melt. This interpretation explains the abundance of polycrystalline diamond in placers. Its sporadic occurrence in diatremes is generally related to the erosion of their uppermost parts.

RESEARCH METHODS

The sample of the polycrystalline diamond aggregate, 1.298 carat in weight, was an object of the complex mineralogical and geochemical study including a detailed observation under a binocular microscope, analytical SEM and TEM, EPR, and INAA investigations. After the standard mineralogical description, the sample was split into a few fragments, which were used for the study of their surface and interiors.

Fragments were studied with a JSM-5300 scanning electron microscope equipped by a Link ISIS energy dispersive spectrometer capable of chemical element determination from Be to U and with a JEM-100C

transmission electron microscope equipped by a KeveX-5100 energy dispersive spectrometer, which enables the determination of elements from Na to U. The suspension specimens for TEM analysis were prepared using the technique reported previously (Gorshkov *et al.*, 1995a). The EPR method was described in (Bershov *et al.*, 1995; Gorshkov *et al.*, 1997).

The INAA method was used for the determination of REE and other elements. After being washed in distilled water, the polycrystalline diamond sample was irradiated in the MIFI experimental nuclear reactor; the subsequent measurements of element contents were carried out in the IGEM laboratory following the standard method (analyst A.L. Kerzin).

RESULTS

Mineralogical Characteristics

The sample studied has an appearance of opaque graphitized fine-grained diamond aggregate irregularly shaped. This appearance fits the bort, i.e., the variety IX diamond classification (Orlov, 1984). The aggregate consists of diamond grains, a few hundredths to 1.5 mm in size, which occupy about 20% of the sample surface, and the cryptocrystalline dark gray cement. The color of diamond grains varies from greenish gray to dark gray; greenish translucent monocrystals, less than 0.1 mm in size, were occasionally noted. The tabular-stepwise character of the face growth is clearly seen in nearly all crystals; the twinned and intergrown crystals, up to 0.7–0.8 mm in size, are rather frequent.

The largest diamond grain, 1.5 mm in diameter, is dark in color and has distinct crystallographic outlines, which correspond to octahedron and rhombic dodecahedron faces. The remainder of crystals does not exceed 0.5 mm in diameter. They are characterized by an irregular shape, occasionally with face relics decorated by growth figures. Etching traces were not detected at the surface.

The sample interior substantially differs from the exterior zones. The surfaces of fresh shear joints are lustrous, light gray, and less graphitized. They have a microgranular texture: the individual grains are devoid of crystalline outlines, face relics, etc.; therefore, the grains are near indiscernible. Based on the appearance of the fresh shear joint, the diamond aggregate is more consistent with the carbonado, i.e., variety X in (Orlov, 1984).

Analytical SEM Data

Based on the SEM study of two sample fragments, the diamond is cryptocrystalline (carbonado type) and incorporates a few faced diamond microcrysts, from 0.1 to 1.5 mm in size (Figs. 1a, 1b). This feature is clearly seen in back-scattered electron (BSE) images (Fig. 1a). Light dots and branched segregations are

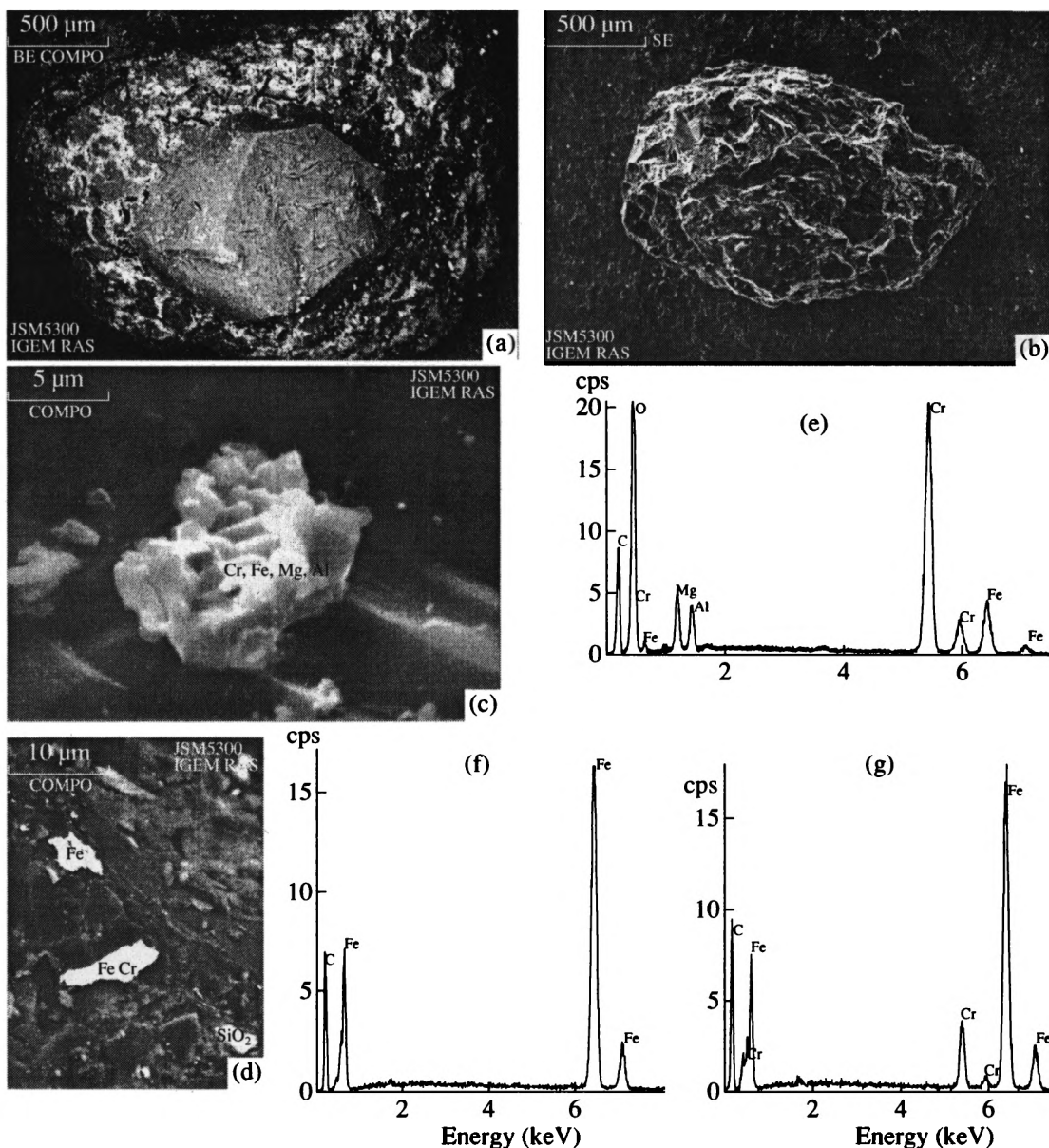


Fig. 1. BSE images: (a, b) two fragments of polycrystalline diamond; (c) chrome-spinel aggregate; (d) α -Fe particle and Fe-Cr intermetallic. Energy dispersion spectra: (e) chrome-spinel; (f) α -Fe; (g) Fe-Cr intermetallic.

mineral inclusions, among which the following minerals can be noticed.

Chrome-spinel. This mineral is commonly represented in BSE images as an aggregate of particles (Fig. 1c). According to energy dispersion spectra (Fig. 1d), they contain Cr, Fe, Mg, and Al. The aggregate surface has no flat sites feasible for the quantitative SEM analysis.

Native iron (α -Fe) was encountered as equant particles, from 1 to 10 μ m in size (Fig. 1e). Only Fe was detected in it (Fig. 1f). The Cr-bearing iron (FeCr solid solution) was also observed as equant and occasionally elongated particles up to 10 μ m in size (Fig. 1e). The

energy dispersion spectrum of one particle (Fig. 1g) reveals Fe and Cr peaks with a predominance of Fe.

Native chromium (Fe-bearing). A triangular particle containing both Cr and Fe is seen in the upper right corner of Fig. 2a. The comparison of characteristic Cr $K\alpha$ and Fe $K\alpha$ radiation intensities indicates the predominance of Cr. The Cr peaks on the energy dispersion spectrum (Fig. 2b) are considerably more intense than the Fe peaks. In addition, a particle of native iron was registered in the image obtained in the characteristic Fe $K\alpha$ image.

Native iron (Ni-bearing) occasionally occurs as an aggregate of equant particles. Its back-scattered elec-

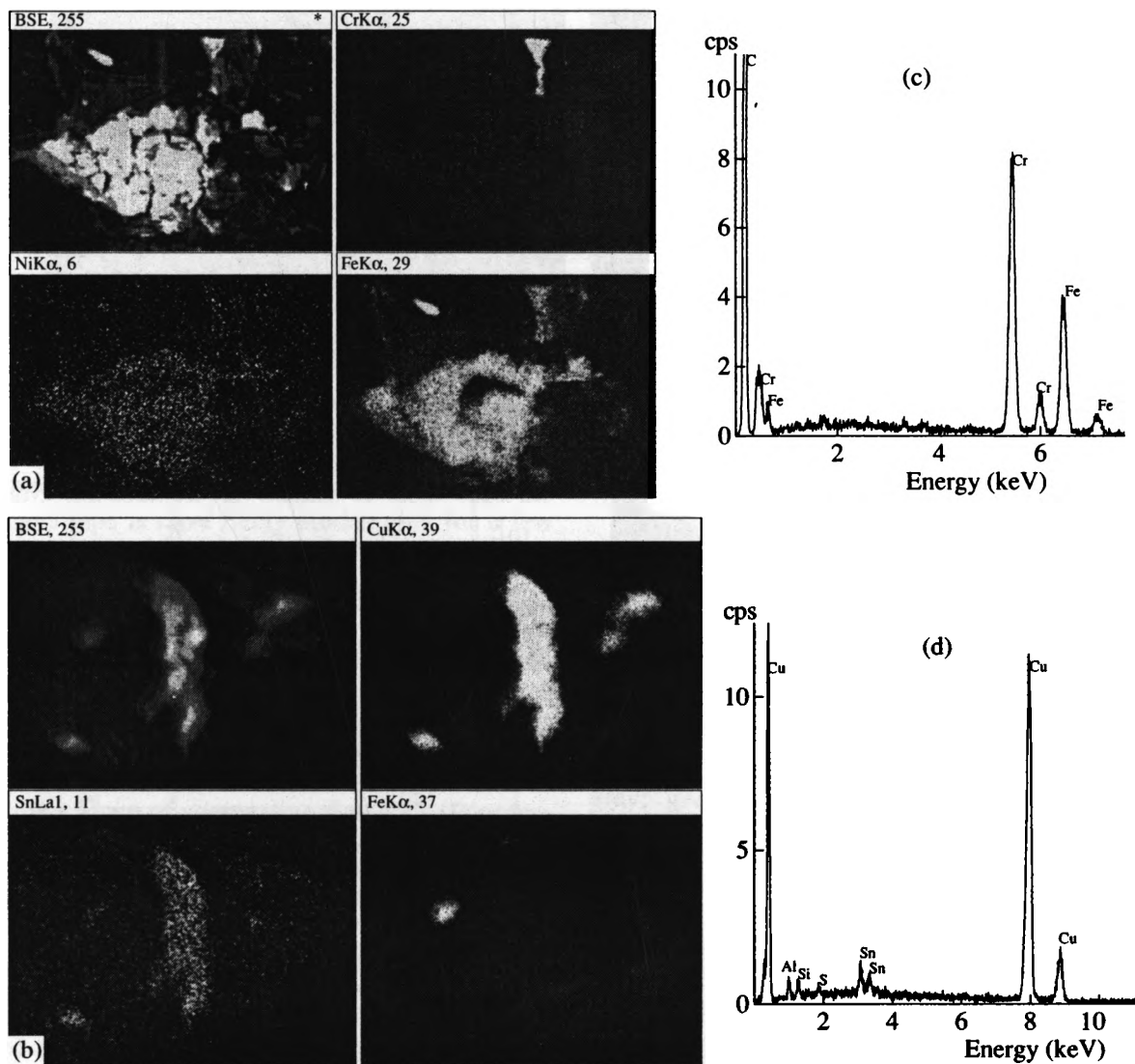


Fig. 2. BSE characteristic radiation and images: (a) native Ni-bearing iron and native Fe-bearing chromium; (b) native Sn-bearing copper. Energy dispersion spectra: (c) Fe-bearing chromium; (d) Sn-bearing copper.

iron image is shown in Fig. 2a. The characteristic Fe K α and Ni K α images (Fig. 2a) confirm the incorporation of Ni into the native iron. Considerably higher intensity of Fe K α radiation than that of Ni K α testifies to the predominance of Fe.

Native copper (Sn-bearing) is represented in BSE images by equant particles, 50–30 μm in diameter (Fig. 2c). The energy dispersion spectrum for one particle (Fig. 2d) shows that Cu peaks are considerably higher than Sn peaks. Images in characteristic, Sn K α , Cu K α , and Fe K α radiations serve as additional evidence in favor of the Sn incorporation into the native copper. What can be seen in the characteristic radiation image of Cu is much more intense than that of Sn, thus

indicating the subordinate amount of Sn. A particle of native iron can be also seen in Fig. 2c.

Native tantalum. The BSE and characteristic radiation (Ta M α and Fe K α) images (Fig. 3a) lead to the conclusion that the Ta particles are closely associated with Fe particles. Because of this, we failed to obtain the energy dispersion spectrum, which would contain only Ta peaks, Fe peaks are always present in the spectra (Fig. 3b).

Thallium chloride (Fig. 3c) is represented in the BSE image as equant particles, 1–12 μm in diameter. The distribution patterns in characteristic O K α , Tl M α , and Cl K α radiations indicate Tl and Cl as components of the particles but the oxygen is lacking. The energy

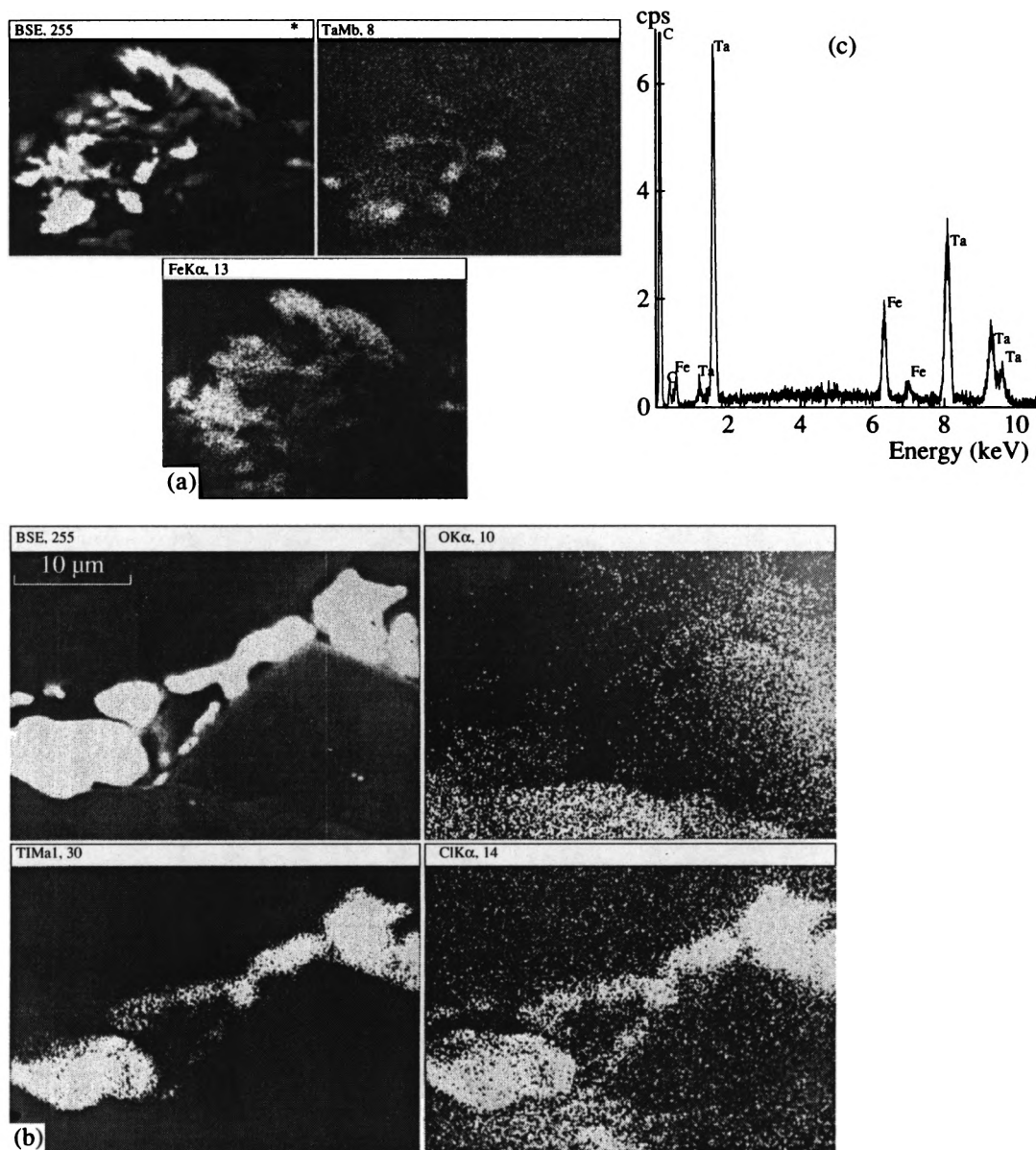


Fig. 3. BSE characteristic radiation and images: (a) native Fe and Ta; (b) TiCl; (c) energy dispersion spectrum of closely associated native Ta and Fe.

dispersion spectrum supports the presence of Ti and Cl only.

Analytical TEM Data

On the TEM images, the diamond is commonly seen as monocrystalline particles, from 1 to 4 μm and more in size (Fig. 4a). Some microcrystals (Fig. 4e) reveal dislocations similar to those reported for the diamond particles in carbonado of the Primor'e region (Seliverstov *et al.*, 1996). In specimen, the particles are most frequently oriented with $(111)^*$ planes parallel to the substrate and perpendicular to the electron beam (Fig. 4b). At the same time, the assemblages of monoc-

rySTALLINE and polycrystalline diamond particles were recognized (Fig. 4c). The electronogram obtained from such aggregate (Fig. 4d) reveals the intense (220) reflections, which correspond to monocrystals in the $(111)^*$ orientation, and the discrete ring 111 , 220 , and 113 reflections related to the polycrystalline component of the aggregate.

Some diamond particles in the (111) orientation are characterized by electronograms, where in addition to the sparse hexagonal net of intense reflections of the cubic diamond depicting its reciprocal lattice plane $(111)^*$, a less distinct net of $hk0$ reflections related to the lonsdaleite were observed. A similar electronogram was reported previously in (Seliverstov *et al.*, 1996). In

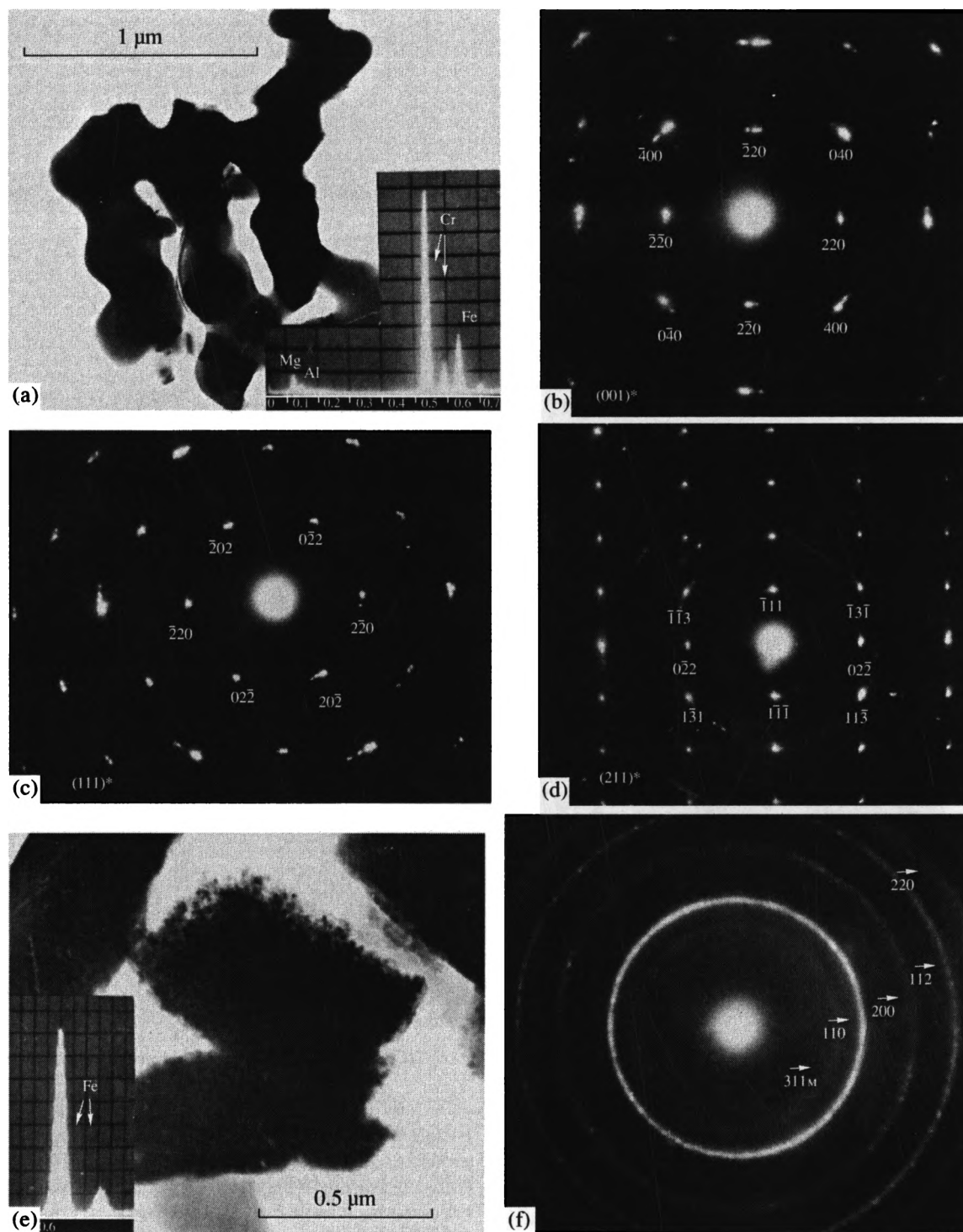


Fig. 5. TEM images and electronograms of chrome-spinel (a, b, c, d) and native iron (e, f) particles; respective energy dispersion spectra are shown in insets.

tices $(120)^*$ for wurtzite and $(123)^*$ for sphalerite are perpendicular to the electron beam.

The above consideration concerning the orientation of wurtzite and sphalerite lattices allowed us to display

the electronogram shown in Fig. 6f. As can be seen, the wurtzite reflections labelled by the B index and the sphalerite reflections labelled by the C index lie on the one straight line, which is parallel to the set of coincid-

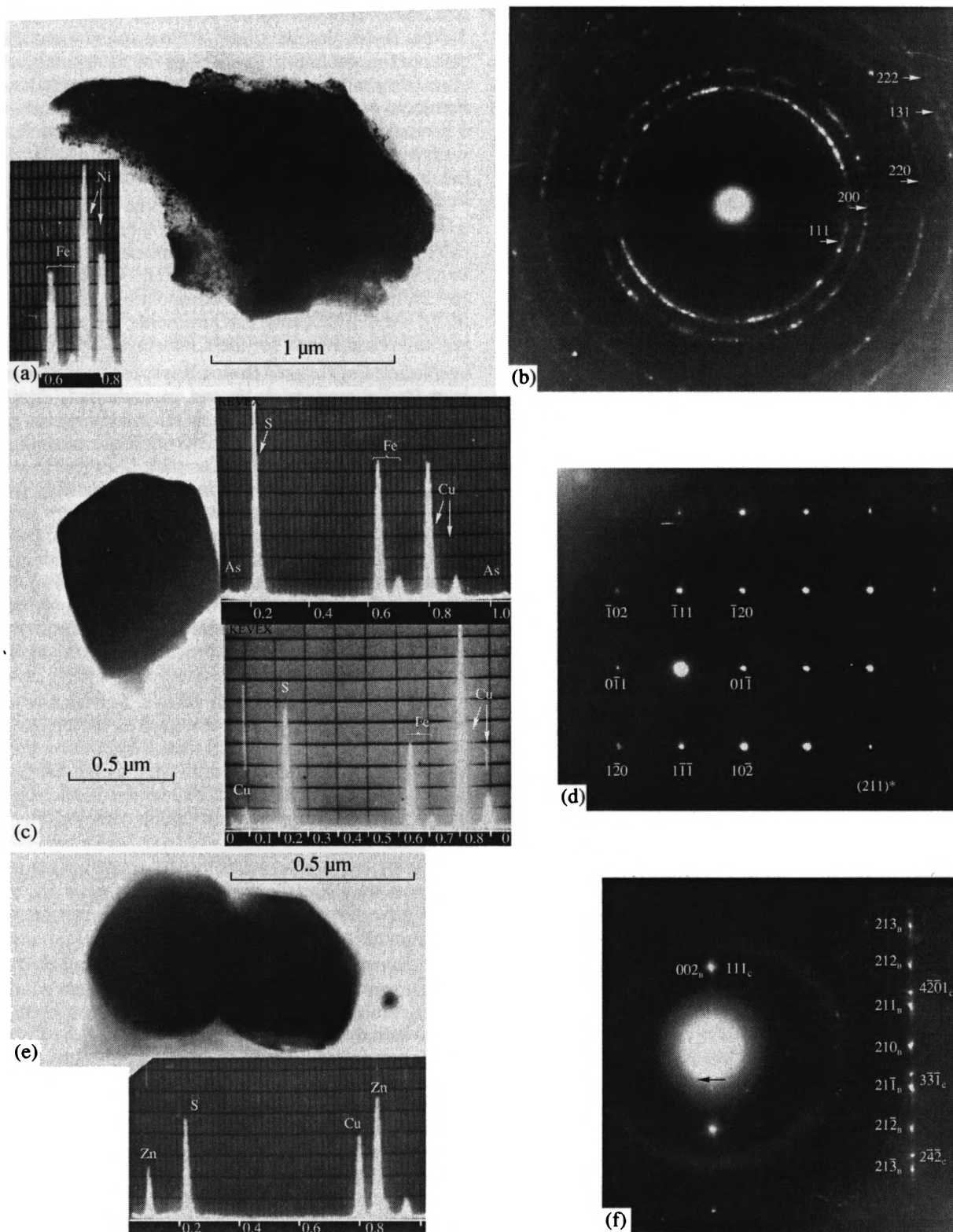


Fig. 6. TEM images: (a) native Fe-bearing nickel; (c) pyrite; (e) wurtzite-sphalerite intergrowth; (b, d, f) respective electronograms; respective energy dispersion spectra are shown in insets (Cu peaks in right parts of spectra are from copper nets of specimens).

ing 00l reflections of wurtzite and 11l reflections of sphalerite. It should be noted that a weak reflection shown by an arrow is caused by a secondary refraction of 21l reflections of wurtzite.

INAA Data

The diamond aggregate is characterized by high Cr and Fe contents (0.6 and 0.3%, respectively) and by appreciably elevated contents of Ba (41 ppm), Zn (22), Co (4.9), Au (0.058), and Ta (0.04). At the same time, the contents of some elements are very low (ppm): LREE (6.9), Th (0.44), and U (0.04). The analytical results were obtained only for La (1.26 ppm), Ce (5.6), and Eu (0.04); the concentrations of other REE are below the detection limit (ppm): Nd (<0.58), Sm (<0.05), Tb (<0.01), Yb (<0.0127), and Lu (<0.0018).

EPR Data

The EPR spectra turned out to be extremely complicated mainly due to the effect of large crystals with irregular orientation. Such spectra may be interpreted only in a case where it is possible to select and analyze an isolated crystal for angular patterns in the spectrum. In our case, such attempts were not assumed, and only isotropic, orientation-independent components belonging to a totality of small crystals were studied in the integrated spectrum. Part of the crystals were related to the R1 center in carbonado, which is inferred to contain Si.

This inference is consistent with the presence of Si in the sample that does not contain silicate or aluminosilicate inclusions. In contrast to the ideal diamond structure, the structure of carbonado with its vacancies can apparently retain the Si atoms in energetically reasonable positions close to vacancies. The P2 centers consisting of three nitrogen atoms were revealed in the EPR spectra, but the signals from isolated nitrogen atoms (centers P1) replacing carbon in the diamond structure were not detected. In addition, the carbonate with the spectrum of Mn^{2+} that replaces Ca^{2+} was recorded.

DISCUSSION

Mineralogical data and results of the electron microscopy indicate a very complicated nature of the diamond aggregate under study. When taking into account the considerable content (about 20 vol %) of relatively large grains (up to 1.5 mm in diameter) it may be referred to as a bort (or framesite) of the variety IX (Orlov, 1984). The size of the fine individual crystals in the groundmass (from tenths to a few μm) is close to carbonado (variety X), and the presence of the lonsdaleite flakes indicates a similarity with yakutite (variety XI).

Our viewpoint is that principal mineral inclusions in the diamond aggregate are syngenetic.

Chrome-spinel is one of the characteristic syngenetic minerals in the diamond of peridotitic affinity. It

was also reported from carbonado (Trueb and Wys, 1971). As is known, the chrome-spinel composition reflects the geological conditions of its formation. The chrome-spinel from ultramafic rocks, e.g. from dunite is commonly characterized by a high Cr content and reveals a severe depletion in Al (Mineraly, 1967). These features were recorded in our case. According to the INAA results, the diamond aggregate contains 0.6 wt % Cr.

The compositions of three chrome-spinel inclusions in African diamonds (Meyer, 1987) allowed their identification as Cr-picotite. The composition of one sample is as follows (wt %): MgO (14.2), FeO (14.5), Cr_2O_3 (67.2), Al_2O_3 (5.12). This composition as well as low SiO_2 , TiO_2 , CaO, and ZnO contents are close to what we have established for the Cr-picotite.

Native Fe, Cr, and their alloys. Inclusions of native iron (α -Fe) previously found in carbonado from the Yakutia and deposits of central Africa were distinguished by a relatively low (2–3 wt %) Cr content (Gorshkov *et al.*, 1995a, 1996). The pure α -Fe and the native iron, which is enriched in Cr to a considerably greater extent than had been reported previously, were detected in the aggregate under study. The Cr-bearing iron is likely an Fe–Cr solid solution. Natural Fe and Cr solid solutions vary in composition from almost pure iron to almost pure chromium, but the Cr content is commonly found in iron and the Fe content in chromium does not exceed 12 wt % (Novgorodova, 1994). Our data is consistent with this statement.

Native Fe, Ni, and their alloys. Particles of native Ni-bearing iron have been revealed in the polycrystalline diamond for the first time. This compound is undoubtedly a solid solution. The native Fe-bearing nickel is also a solid solution, which is close to the native nickel from serpentinite in Fe content (Novgorodova, 1994).

Native copper was previously described in carbonado from the Primor'e region (Seliverstov *et al.*, 1996). The native Sn-bearing copper has been found in the polycrystalline diamond for the first time.

Native tantalum is a very rare mineral; only few findings are known. It was first found in heavy concentrates from the platinum palcer in the central Urals. The native tantalum in Au-bearing placers of the Primor'e region occurred in close association with diamond (Seliverstov *et al.*, 1996). The native tantalum as an inclusion in the polycrystalline diamond is reported for the first time.

The increasing number of native metal findings in diamonds allow their assemblage to be regarded as a regularity. Native metals undoubtedly play the important role in the diamond genesis. In combination with other minerals, the native metals (α -iron, copper, and tenite) were found as central inclusions in the monocrystalline diamond (Bulanova *et al.*, 1986; Bulanova, 1995).

It is suggested that these inclusions might serve as seeds that lower the energetic barrier of the diamond

origination. In polycrystalline diamonds, where the broader associations of native metals are encountered, they might serve as seeds and affect the nucleation rate of the diamond. This is confirmed by experiments on artificial diamond growth with the application of metals (Fedoseev *et al.*, 1984; Orlov, 1984). For example, a method of the diamond synthesis in the graphite-metallic catalyst system is known. Metals, like Cu, Co, Fe, Cr, Pb, etc., used in the diamond synthesis manifest themselves both as solvents and specific catalysts. As a solvent, they bring the isolated atoms and entire graphite blocks into solution. As a catalyst, they diminish the surface energy of the interphase boundary with a carbon particle, thus decreasing the energetic barrier of phase transformation and promoting nuclei formation.

Intergrowths of zinc sulfides (wurtzite and sphalerite), which were recorded in diamonds for the first time, are important in genetic aspects. The wurtzite (β -ZnS) is hexagonal, whereas the sphalerite (α -ZnS) is cubic. Both modifications have tetrahedral coordination of Zn and S atoms where each Zn atom is surrounded by four S atoms and each S atom is surrounded by four Zn atoms. Polytypes with a mixed cubic and hexagonal packing exist. Sphalerite is a low-temperature modification enantiotropically transformed in the β -form (wurtzite) at 1024°C. Oriented intergrowths of various ZnS polytypes, including the sphalerite and wurtzite intergrowth, were reported (Verma and Krishna, 1969). Two versions in interpretation of formation conditions of such intergrowths within the diamond are possible: (1) at a temperature below 1024°C, where the hexagonal wurtzite has overgrown along the (001) plane by structurally similar layers of the cubic sphalerite in the (111) orientation or (2) when wurtzite partly passes into the sphalerite at 1024°C during the diamond cooling.

Thallium chloride (TlCl). This chemical compound was established for the first time as an independent mineral phase not only in diamonds, in particular, but in natural minerals, in general. It should be noted that alkali metal chlorides (K and Na) are revealed in diamonds rather frequently. In particular, the majority of light-colored inclusions in Figs. 1a and 1b are represented by these species. However, they are commonly regarded as technogene impurities, which were incorporated into aggregates during either the specimen preparation or their subsequent investigation. Such interpretation is virtually ruled out for Tl, which is a very rare element, and its compounds are not used in the study. In this connection, it is worth mentioning the recent finding of syngenetic KCl inclusions of cubic shape, 0.2–2.0 μm in size, in the diamond monocrystals from the Shendgli N1 pipe, Shandong province in China (Chen Feng *et al.*, 1992).

Results of the SEM study of the diamond aggregate are consistent with INAA results. The presence of numerous inclusions consisting of native Cr, Fe, Ni, Ta, and zinc sulfides is confirmed by high Cr and Fe con-

tents and by an enrichment in Zn, Ta, and likely in Ni as is inferred from the elevated Co content. Very low REE contents mirror the lack of respective mineral inclusions, which are however, typical of some previously investigated polycrystalline diamonds, e.g., for carbonado from Brazil (Gorshkov *et al.*, 1997).

In spite of a low total sum of REEs in the diamond aggregate, it is characterized by a negative type of the normalized REE pattern, i.e., a distinct predominance of LREE with a La/Yb ratio above 100. Such an REE pattern is typical of kimberlites from the Udachnaya pipe and elsewhere (Kaminskii *et al.*, 1978; Mitchell, 1986). In addition, the diamond aggregate has a nearly chondritic value of Eu/Sm = 0.8, which is characteristic of primary mantle-derived rocks including kimberlites, and indicates the insignificant development of magmatic crystal fractionation (Vinokurov, 1995, 1996).

In terms of the intense development of coupled N–V centers, the polycrystalline diamond aggregate is similar to the previously studied carbonado from the Yakutia and Brazil. At the same time, the P1 centers, which are typical of the majority of carbonado samples, were not detected in EPR spectra. Their lack may be related to a high rate of the aggregate growth. As was established from experimental works on the diamond synthesis, the coefficient of isolated nitrogen capture is inversely proportional to the rate of crystal growth (Samoilovich *et al.*, 1974).

Mineralogical, Geochemical, and Genetic Implications

The comparative analysis of results obtained from our complex study and related data reported in the literature allows us to draw some genetically important conclusions concerning specific mineralogical and geochemical features of the sample investigated (above all, the diamond aggregate structure, chemical and mineral compositions of inclusions, their distribution and abundance) and to discuss in general the formation conditions of polycrystalline diamond.

The diamond aggregate under study has a complicated structure and represents a unique material with structural characteristics of three diamond varieties: bort, carbonado, and yakutite. In contrast to other polycrystalline diamonds (particularly, to previously studied carbonado) with a considerable porosity, this aggregate is massive and virtually devoid of free pores.

The absence of etching traces at monocrystal faces and the absence of clasts in the aggregate indicate an almost simultaneous formation of monocrystals and polycrystalline diamond cement. It should be noted that this aggregate reveals a certain similarity with impact diamonds from the Canyon Diablo, iron meteorite, and some stony ureilites (Vdovykin, 1970).

The combination and distribution of mainly syngenetic inclusions, from fractions of a micrometer to a few tens of micrometers in size, are very peculiar. Judging from SEM, TEM, and INAA results, inclusions of

metals (Cr, Fe, and Ni) are predominant. They are distributed rather uniformly in the groundmass of the diamond aggregate.

The mineral composition of inclusions as a whole is fairly diverse: native metals (Fe, Cr, Ni, Cr- and Ni-bearing iron, Ta), their oxides (chrome-spinel and magnetite), sulfides (pyrite, As-bearing pyrite, wurtzite, sphalerite), and chlorides (TlCl), but the native metals and their alloys are most abundant. It should be noted that the silicate or aluminosilicate inclusions, e.g., olivine and pyroxene, were not detected in the diamond aggregate even in the most careful study with an electron microscope. At the same time, these minerals are typical of inclusions in diamond monocrystals from kimberlites and mantle-derived nodules.

The mineral composition of main inclusions closely resembles the small and newly formed minerals in reaction zones around polycrystalline intergrowths of diamond and graphite from stony meteorites (ureilites). According to Vdovykin's (1970) data, these minerals are represented by a Ni-bearing iron (kamacite), troilite (FeS), and chromite, i.e., by native metals, sulfides, and oxides.

Judging from abundant and diverse microinclusions (native metals, their alloys, oxides, sulfides, and chlorides), the diamond aggregate was formed under conditions of extreme thermodynamic disequilibrium with drastic temperatures and pressure differences. This is confirmed by the above-mentioned intergrowths of wurtzite and sphalerite with a difference in formation temperatures of more than 700°C. Such decompression conditions are most typical of near-surface explosions, both exogenic and endogenic.

The near-surface formation of the diamond aggregate is indicated by a mode of aggregative diamond occurrence in the Udachnaya pipe. They are concentrated in the uppermost part of the kimberlite section related to the first phase of emplacement and distinguished by the maximum abundance of sedimentary rock fragments and the depletion in eclogite and peridotite xenoliths. This is also confirmed by a presence of mantle-derived (Cr, Fe, Ni, etc.) and crustal (Ba, Zn, Au, etc.) impurities in the diamond aggregate and by REE patterns, which are similar to those in host kimberlites.

Thus, principal genetic implications for the polycrystalline diamond from the Udachnaya pipe are as follows. It was formed under a decompression environment from a C-oversaturated gaseous phase enriched with metals, which served as catalysts and crystallization centers that were retained as various microinclusions. It is likely that the cluster carbon compounds (fullerenes) were a plausible species of gaseous carbon. According to experimental data, the fullerenes are most appropriate compounds, both in temperature and pressure, for the diamond crystallization as compared with other carbon species and compounds (Vinokurov *et al.*, 1997).

From this standpoint, the specific structural features of the diamond aggregate may be explained, in particular, the presence of lonsdaleite flakes can be understood. Experimental data indicate the possibility of lonsdaleite formation without external pressure (Seli-verstov *et al.*, 1996). Experiments reported in (Chai-kovskii and Rozenberg, 1984), the diamond crystallites with lonsdaleite were obtained by a precipitation of gaseous carbon at a cooled substrate, where the lonsdaleite was formed as a transitional variety that was transformed into diamond after an additional uniform heating of the sample. Hence, the presence of lonsdaleite may indicate not only the condition of diamond crystallization but also the character of subsequent thermal regime.

We suggest that the decompression scenario of polycrystalline diamond formation is a most plausible mechanism under natural conditions. This mechanism may be applied to the similar (in thermodynamic regime) near-surface explosion structures related to both exogenic (astroblemes) and endogenic (diatremes, volcanoes, etc.) processes. Therefore, Marakushev (1996) regarded classical astroblemes of the diamond-bearing Puchezh-Katun and Popigai impact-ring structures as results of endogenic explosions. In this connection, the polycrystalline diamond (carbonado, as follows from our previous study) in basalts from the Avacha group of volcanoes in the Kamchatka should be noted. The origin of this diamond is most likely related to explosion structures (Gorshkov *et al.*, 1995b).

The clastic carbonado from placers, which have been studied by us and other researchers, differs in some specific features from the above diamond aggregate. First of all, the case in point is a significant porosity of carbonado. In addition to typical primary inclusions, there are numerous microcavities filled with hydrothermal and supergene minerals (Gorshkov *et al.*, 1995a, 1995b, 1996, 1997).

Specific features of clastic carbonado are apparently caused by superimposed endogenic and exogenic alterations at the place of their primary formation in diatremes and other explosion structures, and by a subsequent supergene alteration during the bedrock erosion and the placer formation. These processes give rise to the intense oxidation of numerous inclusions of native metals and their compounds, which is accompanied by their leaching and replacement by various epigenetic minerals oxides and hydroxides (of iron and manganese aluminophosphates, etc.).

At the same time, the clastic polycrystalline diamonds, which are substantially distinct in the structure, and the inclusion composition from native varieties, retain some common mineralogical and geochemical characteristics, which can be used for the recognition of their provenances. However, it should be noted that the presence of lonsdaleite is not a unequivocal criterion, which would indicate the genetic relations to exogenic impact structures (astroblemes).

Reliable indicators of genetic links between the clastic polycrystalline diamonds and native sources should take into account the character of syngenetic inclusions and the distribution of REE and other elements. These typomorphic features are substantially different in specific districts.

This statement may be illustrated by previously obtained results on polycrystalline diamonds from a melanocratic basalt (avachite) in Kamchatka and from placers of the Primor'e region (Gorshkov *et al.*, 1995b; Seliverstov *et al.*, 1996). A similar combination of specific microinclusions (native Si, Fe, and Al, silicon carbide, rutile, etc.) along with the total absence of Cr-bearing minerals indicate that melanocratic volcanics might be a source of clastic polycrystalline diamond in placers.

On the contrary, polycrystalline diamonds of the Yakutian province kimberlites substantially differ from the above-described species in composition of mineral inclusions (native Cr, Fe, and Ni and their alloys, sulfides and oxides) and in the REE patterns (enrichment in LREE), yet are similar to those of the kimberlite. It is evident that the clastic polycrystalline diamonds from placers must inherit these mineralogical and geochemical characteristics.

CONCLUSION

This complex study of the diamond aggregate from the Udachnaya pipe, the Yakutian province allows us to establish its specific structure and inclusion composition, the REE patterns and the distribution of other elements. In contrast to previously studied polycrystalline diamonds mainly derived from placers, the sample under study is unique and consists of three diamond varieties.

The cryptocrystalline aggregate is characterized by a great diversity of syngenetic inclusions (native metals and their alloys, oxides, sulfides, and chlorides), an enrichment in some chemical elements and a REE pattern typical of kimberlite. This testifies to the thermodynamic disequilibrium of its formation and to the presence of both mantle and crustal components.

The diamond aggregate was formed during the emplacement of the first portion of kimberlitic melt under thermodynamic disequilibrium conditions with drastic differences in temperature and pressure, these are typical of decompression environments in near-surface explosion structures. The diamond crystallization most likely occurred from a C-oversaturated gaseous phase enriched in metals, which served as catalysts and crystallization centers.

The decompression environment of the polycrystalline diamond formation pertains to near-surface explosion structures of both the exogenic (astroblemes) and the endogenic (diatremes, volcanoes, etc.) types, which are similar in the thermodynamic regime.

The abundance of diamond aggregates in the early kimberlite of the Udachnaya pipe and their inferred wide occurrence in upper parts of some other pipes of the Yakutian province lead to the suggestion that kimberlite erosion and the partial disintegration of aggregates might give rise to placers containing appreciable amounts of polycrystalline diamonds (carbonado and yakutite) along with other varieties.

The mineral composition of microinclusions and the distribution of REE and other elements may be used as reliable indicators of genetic relations of clastic polycrystalline diamonds to certain native sources.

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The Upper Riphean Stromatolitic Reefal Complex: Burovaya Formation of the Turukhansk Region, Siberia

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Abstract—This work presents the first detailed description of the lithostratigraphy and facial structure of the lower section of the Upper Riphean Burovaya Formation, which representing a thick (up to 1000 m) carbonate sequence separated by an erosional nonconformity into two subformations. The lower subformation (80–500 m), composed of the pelitomorphitic, clastic, and stromatolitic complex of limestones and dolomites, includes small reefs. It is divided into four members. The lower three members are relatively continuous in the area, whereas the fourth member rapidly changes (in composition and thickness) in the lateral direction. The upper subformation (380–580 m) combines the intricate reefal and cover complexes. The reefal complex is represented by a huge (thickness up to 500 m, width 15–20 km, length up to tens of kilometers) stromatolite reef and a deep-water, fine-grained, partially condensed and lumpy, carbonate rim. The reef consists of the relatively shallow-water bioherms and biostromes of columnar and stratiform stromatolites along with large (hundreds of meters across) deep-water dome-shaped buildups with horizontal accretion. The cover complex (up to 130 m) is composed of shallow-water clayey-carbonate sediments that conformably overlie the perireefal sediments and the reef periphery. The Burovaya Formation is divided into ten facial rock associations, and some of the associations comprise several facies. Based on the composition and spatial distribution, environments and evolution pattern of the Upper Riphean basin are reconstructed, and major event boundaries are ascertained and interpreted in terms of the sequence stratigraphy.

INTRODUCTION

At early stages of the study of Precambrian stromatolites, they were occasionally considered possible reef-builders (Twenhofel, 1919; Fenton and Fenton, 1931). However, the opposite concept dominated until the end of the 1970s and suggested that geomorphologically distinct biogenic buildups could not exist in Precambrian basins without reef-forming skeletal organisms. This opinion was promoted by inadequate sedimentological study of Precambrian carbonate platforms and highly popular notions, according to which the passive trapping and binding of the allothigenic carbonate particles by cyanobacterial communities was the main and sole process of stromatolitic accretion (Serebryakov, 1975; Monty, 1973, 1977). This concept was responsible for the *a priori* inferences about low lifetime (synoptic, according to Hofmann, 1969) relief of both individual stromatolites and their aggregates.

A breakthrough in the resolution of the problem of the Precambrian reef formation was noted at the end of the 1970s–mid 1980s as a result of a publishing of the first persuasive descriptions of Proterozoic stromatolite reefs (Hoffman, 1974; Serebryakov, 1975; Donaldson, 1976; Cecile and Campbell, 1978; Grotzinger, 1986a, 1986b; Beukes, 1987), including giant buildups (Aitken *et al.*, 1979, 1982; Aitken, 1981). Under the influence of Russian researchers (Maslov, 1960, 1961; Serebryakov and Semikhatov, 1974; Serebryakov, 1975; Krylov, 1975, and references therein), the active role of

the stromatolite-building microbial communities in the carbonate material precipitation was accepted (Walter, 1976; Semikhatov *et al.*, 1979). Later works ascertained the specifics of Precambrian carbonate accumulation and revealed a wide distribution of early marine carbonate cement in stromatolitic environments of that time (Geldsetzer *et al.*, 1988; Grotzinger, 1989; Sami and James, 1996).

In recent years, the number of Precambrian stromatolite reefs revealed has considerably increased. Among them, researchers have ascertained morphological analogues of most types of reefs known in the Phanerozoic (Geldsetzer *et al.*, 1988; Turner *et al.*, 1993, 1997; Narbonne and James, 1996; and others). The Proterozoic reefs of North America served as major objects of study, while the Eurasian Riphean sediments, which are significantly more enriched in stromatolites, were neglected. The morphology of a few stromatolite bodies in Riphean sediments has been described (Serebryakov, 1975; Khabarov, 1985, 1987, 1990; Khabarov and Tanygin, 1991; Olovyanishnikov, 1997; Petrov and Semikhatov, 1997). However, only a part of these bodies can be recognized as the reefs proper, i.e., the geomorphologically distinct biogenic buildups.

This work is an attempt to eliminate the shortcoming in knowledge of stromatolite reefs in Siberia, present the description of a giant reef from the Upper Riphean Burovaya Formation in the Turukhansk region, demonstrate the position of this reef in the gen-

eral succession of the Burovaya sediments, and reconstruct the evolution of the sedimentary basin.

GEOLOGICAL SETTING, AGE, AND LITHOSTRATIGRAPHY OF THE BUROVAYA FORMATION

The Turukhansk region, which corresponds to one of the marginal uplifts of the Siberian Platform, reveals outcrops of the Riphean and unconformably overlying Vendian sediments within the Phanerozoic field (Fig. 1). Riphean sediments compose three tectonic blocks that are restricted by low-angle faults (thrusts and reverse thrusts), meridionally extended, and displaced to the east, i.e., toward the Siberian Platform (Dragunov, 1963; Komar and Serebryakov, 1969; Serebryakov, 1975; Shenfil', 1991). In the eastern (Golyi Yar) block, the Riphean deposits have a commonly gentle (15° – 35°) dip toward the west. Only along its northwestern edge, in upper reaches of the Kamennaya River, one can observe a small fault-zone anticline with a steep (70° – 90°) eastern limb. On the south, in lower reaches of the Sukhaya Tunguska River, deposits form a flat large antiform. The borehole (i.e., Burovaya, in Russian), drilled on the antiform crest in 1939, revealed hydrocarbon pools in the rock sequence (Kirichenko, 1940a, 1940b; Gusev, 1941; Dragunov, 1959). Therefore, the rock sequence has been named the Burovaya Formation. The central (Turukhansk) block represents an asymmetric syncline with a gentle (10° – 40°) eastern limb and a subvertical western limb. In central and northern zones of the region, the western limb is cut by a submeridional fault. The western (Durnoi Mys) block is exposed as a narrow, westward-inclined monocline extending along the right bank of the Yenisei River, near the Nizhnyaya Tunguska River mouth. The afore-said blocks are complicated by minor subsidiary (relative to major reverse thrusts) submeridional faults, low-amplitude sublatitudinal strike-slip faults, and small shears without any appreciable displacement of layers. Vendian rocks, preserved at the present denudation level within two eastern blocks, unconformably overlie different Riphean formations, including the Burovaya Formation.

The Burovaya Formation, up to 1000 m thick, is located near the middle section of the Riphean succession in the Turukhansk region (Fig. 1). It has conformable contact with the underlying clayey-carbonate section (Derevnya Formation) and unconformable contact with the overlying sandy-shaly package of carbonate rocks (basal section of the Shorikha Formation). The Burovaya Formation is composed of dark gray and black (fine-grained), as well as gray (predominantly, clastic and stromatolitic) dolomites and limestones. The fine-grained varieties have a specific molar-tooth structure, i.e., a dense network of fine syneresis cracks infilled with veinlets of white crystalline carbonate material (Kirichenko, 1940; Gusev, 1941; Dragunov, 1959, 1963; Semikhatov, 1962).

The age of the Burovaya Formation is based on concordant isotope-geochronological, paleontological, and chemostratigraphic data. The isochron Pb–Pb age of carbonate rocks in the Sukhaya Tunguska Formation, which underlies the Derevnya Formation, is 1035 ± 60 Ma (Ovchinnikova *et al.*, 1995), while the K–Ar datings of glauconites from various Riphean formations of the Turukhansk region show that these sediments underwent epigenetic alteration 800–850 Ma ago (Semikhatov and Serebryakov, 1983; Gorokhov *et al.*, 1995; and references therein). The latter inference is corroborated by the chemostratigraphic C-isotope data suggesting that the Turukhansk Riphean succession lacks sediments younger than 850–800 Ma (Knoll *et al.*, 1995). According to V.N. Sergeev, silicified microfossils of the Burovaya Formation contain, in addition to long-ranged taxa, the rare *Polysphaeroides* that are common in the Upper Riphean. Stromatolites of this formation contain *Baicalia lacera* Semikh. (Semikhatov, 1962; Shenfil', 1991), which is typical for the lower Upper Riphean of Siberia and North Africa (Knoll and Semikhatov, 1998). Meanwhile, the subjacent Derevnya Formation contains acanthomorphic acritarchs *Trachyhystrichosphaera aimica* Herm., *T. stricta* Herm., and *Prolatoforma aculeata* Mirk. (Petrov and Veis, 1995), which are typical for the Upper Riphean (Knoll and Sergeev, 1995), and stromatolites *Inzeria tjomusi* Kryl. and *Jurusania cylindrica* Kryl., which are typical for the lower section of this erathem (Krylov, 1975). Thus, the Burovaya Formation, dated within a range of 1035 ± 60 to 800 Ma, is assigned to the lower Upper Riphean.

The lithostratigraphy and boundaries of the Burovaya Formation are controversial (Kirichenko, 1940; Semikhatov, 1962; Dragunov, 1963; Khomentovskii *et al.*, 1972; Serebryakov, 1975; Kozlov *et al.*, 1988; Shenfil', 1991; Petrov and Veis, 1995). Here, the lower boundary of this formation is drawn along the level where dark gray, parallel and wavy-laminated, sometimes stromatolitic dolomites, which terminate the Derevnya Formation, are replaced by dark dolarenites in the eastern zone and clastic and stromatolitic limestones and dolomites in the western zone. This replacement corresponds to the beginning of transgression that terminated at later stages of the early Burovaya time. We draw the upper boundary along the base of the sandy-shaly unit (thickness from 3–6 to 46–50 m) that overlies different horizons of the Burovaya Formation and begins the Shorikha Formation. The sections studied characterize the Burovaya Formation over its entire domain (Fig. 1). However, the Kamennaya River section near the waterfall is not described here, because the secondary alterations and poor exposure of rocks did not allow us to differentiate this section in a detailed fashion.

The Burovaya Formation is separated by a sharp erosional boundary into two subformations. The upper subformation is preserved after the Pre-Vendian erosion event only in the central and northern zones of the Turukhansk region (Fig. 2). The lower subformation is

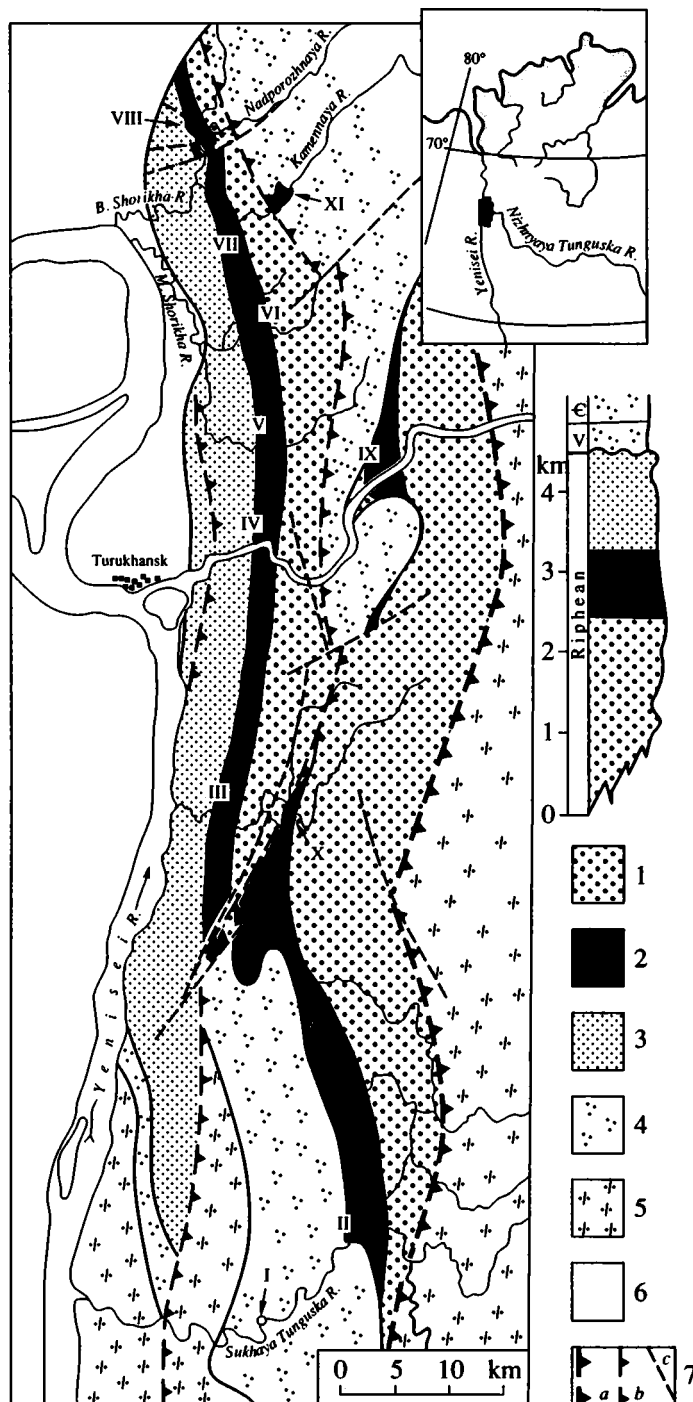
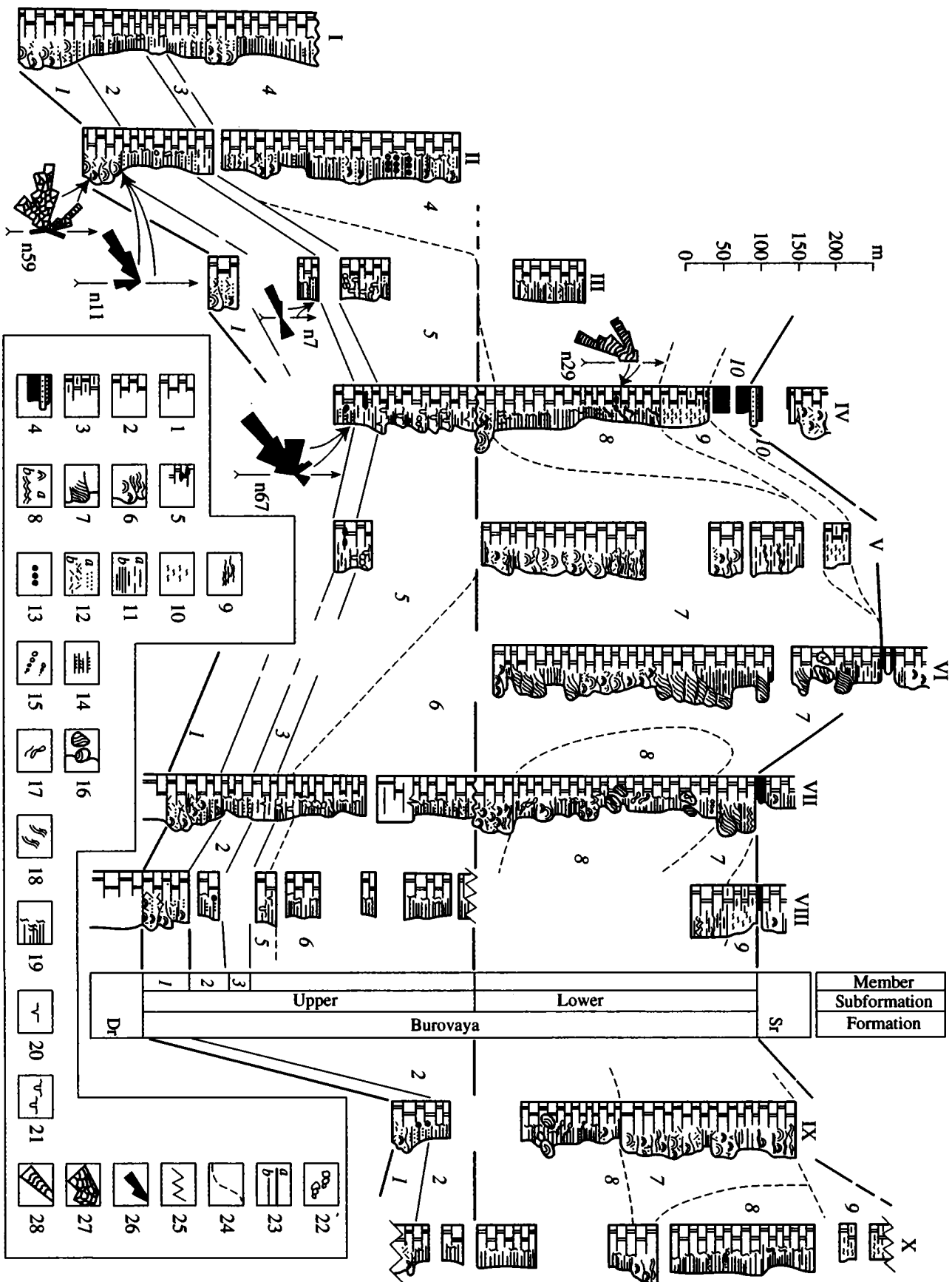


Fig. 1. Schematic geological setting of the Turukhansk region and location of the Burovaya Formation sections. Stratigraphic subdivisions: (1) Middle and Upper Riphean sediments underlying the Burovaya Formation, (2) Upper Riphean Burovaya Formation, (3) Upper Riphean sediments overlying the Burovaya Formation, (4) Vendian (Platonovskaya Formation), (5) Lower Paleozoic, (6) Mesozoic; (7) faults: (a, b) major reverse-thrusts: (a) marginal Voronov, (b) the others, (c) minor.

The Burovaya Formation sections studied: (I) borehole in lower reaches of the Sukhaya Tunguska River (adopted from Gusev, 1941), (II) Sukhaya Tunguska River in the Tabornaya River mouth area, (III) middle reaches of the Miroedikha River, (IV) Nizhnyaya Tunguska River below the Strel'nye mountains, (V) upper reaches of the Malaya Shorikha River, (VI) Bolotnaya River and Maiskii Creek, (VII) lower reaches of the Kamennaya River, (VIII) Nadporozhnaya River mouth area, (IX) Nizhnyaya Tunguska River below the Gremyachii Creek mouth, (X) upper reaches of the Miroedikha River, (XI) Kamennaya River near the waterfall.

Stratigraphic indices: (V) Vendian; (Є) Cambrian.



divided into four members. The lower three members are conformable and stable (in composition) over the entire area, while the facies-variable fourth member is preceded with a hiatus in the central and northern zones. Member 1 is composed of dark gray to black (clastic, stromatolitic, and rare pelitomorph) limestones and dolomites. Its thickness ranges from 45 to 80 m, the greater thickness being observed on the southwestern side. Member 2 is marked by the prevalence of dark gray (pelitomorph and clastic) dolomites. Its complete sections are only encountered in the southern zone of the Golyi Yar block along the Sukhaya Tunguska River, where the thickness is as much as 100 m, and in the northern zone of the Turukhansk block along the Kamennaya River, where the thickness is reduced to 45–50 m. Member 3 is represented by light gray dolomites (20–25 m). In the northern areas, its upper part is characterized by the presence of syngenetic breccia, desiccation cracks, and erosion traces. Member 4 consists of clastic, stromatolitic, and fine-grained carbonates in the south (more than 330 m), brecciated to laminated dolomites and limestones in the center (140 m), and a thin (25 m) package of the same dolomites and a thick (250–270 m) sequence of black bituminous dolomites in the north. The total thickness of the lower subformation is greatest (more than 520 m) in the southern zone of the Golyi Yar block and rapidly diminishes to 80–100 m in the central and northern zones. In the Turukhansk block, the thickness is about 250–300 m in the central zone and 400–450 m in the northern zone.

The upper subformation (380–580 m) is composed of two unequal sections. The greater (lower) section comprises the predominant light gray stromatolitic dolomites and limestones, which compose a large reef (thickness up to 500–530 m), and the subordinate reef-rimming dark pelitomorph, clastic-lumpy, and stromatolitic carbonates (220–400 m). The lesser (upper) section, up to 130 m thick, consists of the major clayey dolomites and limestones and the subordinate shales, which overlie the reefal and perireefal sediments and locally pinch out.

FACIAL STRUCTURE AND FORMATION CONDITIONS OF THE BUROVAYA FORMATION

The Burovaya Formation is divided into three facial complexes. The lower subformation consists of only one complex, whereas the upper subformation is composed of two complexes. Each complex incorporates specific facial associations that represent distinct combinations of various lithotypes, among which certain autonomous facies can be recognized. As in our previous publications (Petrov, Semikhatov, 1997, and references therein), the names of associations and facies are based on the characteristic features of the predominant sediment type.

Facial Complex of the Lower Subformation

This complex is subdivided into six facial associations: (1) the clastic-bioherm association, (2) the pelitomorph and granular dolomite association, (3) the parallel and wavy-laminated dolomite association, (4) the fine-grained, stromatolitic, and clastic dolomite association, (5) the brecciated and laminated dolomite-limestone association, and (6) the dark molar-tooth dolomite association. The associations 1–3, connected by gradual transitions, make up continuous bodies in the lower three members of the lower subformation. The associations 4–6, which laterally replace each other within the upper (fourth) member, are separated from the subjacent bed by an erosion boundary in the northern and central zones.

(1) The **clastic-bioherm association**, which represents member 1 of the lower subformation, is composed of the major stromatolite bioherms of dolomite and limestone composition along with the subordinate clastic and pelitomorph carbonates. Based on the dimension of bioherms, as well as their relative role in the Turukhansk block and the southern Golyi Yar sections, this association is subdivided into two facial types.

The first facial type, which composes the lower part of the association, represents large contiguous bioherms, up to 100 m long and 10 m thick, separated by 0.5–3-m-thick layers of clastic and very rare pelitomorph limestones and dolomites. The bioherm base is

Fig. 2. Lithostratigraphy and facial associations of the Burovaya Formation. (1–5) Rocks: (1) dolomites, (2) limestones, (3) clayey dolomites and limestones, (4) shales, sandstones, and siltstones (siliciclastics), (5) cherty concretions; (6–8) stromatolite buildups: (6) bioherms and biostromes, (7) large domes with subvertical limbs, (8) typical forms: (a) *Conophyton* and *Jacutophyton*, (b) *Thysagietacea*; (9–20) typical features of rocks: (9) microbial lamination in carbonates, (10) microlamination disturbances in the laminated clayey limestones, (11) horizontal lamination: (a) thick, (b) thin, (12) clastic carbonates: (a) dolocarenites and calcarenites, (b) grainstones and flakestones, (13) oolites, (14) graded bedding in fine-grained sediments, (15) slump breccia, (16) avalanche boulder sediments, (17) small-scale soft sediment deformation of layers, (18) large slump folds, (19) molar-tooth structures, (20) desiccation cracks; (21) karst surfaces; (22) dissolution breccia; (23) lithostratigraphic subdivision boundaries: (a) formations and subformations, (b) members and units; (24) facial boundaries; (25) faults; (26–28) rose diagrams of the orientation of: (26) cross-lamination dip, (27) stromatolite buildup inclination, (28) overturned crests of slump folds.

(I–X) sections studied (see Fig. 1). Facial associations: (1) clastic-bioherm; (2) pelitomorph and granular dolomite; (3) parallel and wavy-laminated dolomite; (4) fine-grained, stromatolitic, and clastic dolomite; (5) brecciated and laminated dolomite-limestone; (6) dark-colored molar-tooth dolomite; (7) reefal; (8) perireefal; (9) clayey striated-laminated limestone-dolomite; (10) variegated shales. Indices: (Dr) Derevnaya Formation; (Sr) Shorikha Formation.

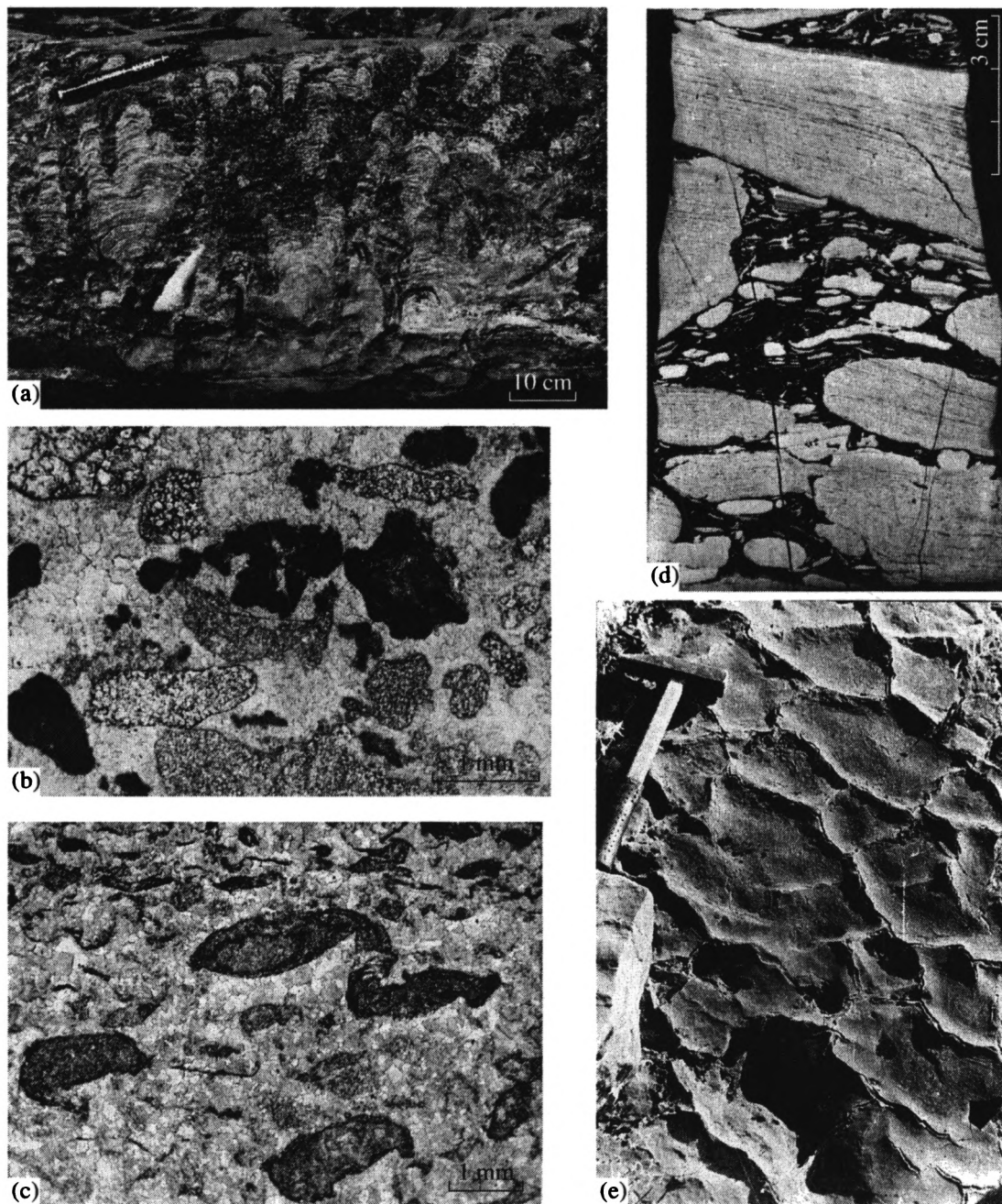


Fig. 3. Some facial features of sediments of the lower subformation of the Burovaya Formation. (a) Small bioherm *Baicalia* in the upper part of the clastic-bioherm association, Sukhaya Tunguska River, photograph of outcrop; (b) intraclastic calcarenites of the clastic-bioherm association, Sukhaya Tunguska River (two types of clastic grains within dolosparite cement: irregular black grains are disintegrated micritic laminae of stromatolites, whereas gray rounded grains are products of lithoclast destruction), thin section; (c) doloarenites of the fine-grained, stromatolitic, and clastic dolomite association, Sukhaya Tunguska River, thin section; (d) dissolution breccia in the brecciated and laminated dolomite-limestone association, Nizhnyaya Tunguska River below the Strel'nye mountains, polished section; (e) dessication cracks in the brecciated and laminated dolomite-limestone association, Nizhnyaya Tunguska River below the Strel'nye mountains, photograph of bedding surface.

marked by erosional surfaces with relief amplitude up to 1.5–2.0 m (Serebryakov, 1975, Fig. 24) and local lenses of fine-grained clayey-carbonate rocks in depressions. The relationship to host deposits suggests that the synoptic relief of bioherms was as much as 3.0–

3.5 m. Stromatolites are composed of the predominant large (diameter 5–15 cm) columnar branching *Baicalia* and *Tungussia* confined to the lower and middle horizons of bioherms. Columnar-stratiform forms prevail in upper horizons, while stratiform varieties are predomi-

nant near the top of bioherms. At the base of several bioherms, one can observe the inclined and subhorizontal columns that are approximately parallel to the cross-lamination dip direction of the associated clastic carbonates (Fig. 2).

The second facial type, which composes the upper part of the association, is represented by the intraclastic calcarenites and small (0.2–3.5 m across and 1.5–2 m thick), isolated, bun-shaped bioherms that consist of small *Baicalia* and lack erosional surface at the base (Fig. 3a).

The clastic part of both facial types is composed of unsorted intraclastic doloarenites, calcarenites, and calcirudites¹ with a coarse horizontal and cross lamination. The majority of fragments are composed of scraps of stromatolite laminae (stromaclasts, according to Sami and James, 1994) scattered in the carbonate gravel–sand matrix. The latter is made up of the irregular micritic grains, i.e., products of stromatolite laminae disintegration, rounded sparitic grains formed during the destruction of lithoclasts (Fig. 3b), and a minor admixture of the siliciclastic silt–sand material.

In the central and northern zones of the Golyi Yar block, where the facial types are not distinguished, the clastic-bioherm association is predominated by the well-rounded grainstones and doloarenites that are occasionally enriched in oolites, while the coarse-clastic carbonates and stromatolites almost disappear. The thickness of sediments increases from 45 in the southwest to 80 m in the west.

Regardless of the morphology, the most of stromatolites of this association are typical for the *Baicalia rara* Semikh. microstructure. The microstructure, which is typical for *B. lacera* Semikh., is only occasionally observed in certain buildups or their fragments (Semikhatov, 1962). The first microstructure is a result of the trapping and binding of the size-variable (up to 0.25–0.3 mm), clastic carbonate (micritic) particles by cyanobacterial mats, while the second microstructure does not contain clastic material and represents the carbonate material precipitation onto the surface or within cyanobacterial mats owing to the metabolic activity of microorganisms (Knoll and Semikhatov, 1998).

This association was formed in variable (in time and space) but hydrodynamically active shallow-water environments. The shallowest (up to intertidal) conditions were developed in the central and northern zones of the Golyi Yar block, while the upper subtidal conditions prevailed in the remaining area.

During the accumulation of the first facial type, relatively deep-water conditions existed in the northwestern zone (northern sections of the Turukhansk block) where traces of the subaerial exposure of sediments are absent and the amplitude of the synoptic relief of bioherms is maximum. Meanwhile, the southern zone

(southern sections of the Golyi Yar block), where the lithological record of short-period oscillations of sea-level were most distinct, was characterized by the formation of an erosional surface with a rugged relief during maximum shallowing under subaerial environments. At the beginning of flooding, the lower horizons of stromatolite bioherms appeared. As the basin deepened, bioherms were rapidly expanded in adjacent depressions partly filled with clastic carbonate sediments of the pelite–silt and sand–gravel dimensions. The coincidence of cross-bedding orientation in sediments and the inclination of stromatolite columns at the base of bioherms (Fig. 2) suggest that a common system of tidal currents existed at the beginning of the development of stromatolite buildups. The lack of any predominant azimuth orientation of columns in the overlying parts of bioherms indicates that bioherm growth was followed by a breakup of the common current system. Judging from the morphology of stromatolites and the composition of associated carbonates, the middle horizons of bioherms likely corresponded to local flooding maximums, while the upper horizons were formed during the initial period of shallowing when hydrodynamic activity was probably attenuated by the screening effect of bioherms. During the shallowing maximum, bioherm growth ceased, but traces of erosion are absent even at the top of the largest stromatolite bodies.

During sediment accumulation of the second facial type, the depositional environment differences between the northwestern and southern zones were leveled, and hydrodynamically active environments of the lower subtidal zone were established over a major area of the Turukhansk region, except at the northeastern shallow-water zone (the central and northern sections of the Golyi Yar block). The typical combination of small isolated bioherms with the predominant intraclastic carbonate sediments likely suggests that the disintegration of stromatolite buildups was more intensive than their accretion during this time. On the whole, the clastic-bioherm association corresponds to a gradual deepening stage of the basin that replaced the shallow-water basin of the late Derevnaya time.

(2) The **pelitomorphic and granular dolomite association**, which makes up member 2 of the lower subformation, is represented by a succession of pelitic–silty and clastic sandy carbonate sediments, in which the grain size increases upward the section. The lower section is mainly composed of pelitomorphic and fine-grained, dolomitic and occasionally calcareous, organic-rich sediments with a fine (0.5–2.0 cm) horizontal, commonly graded bedding. In the southern sections, these rocks include several interlayers of massive bituminous dolomicrosparites. The fine-grained and pelitomorphic varieties are crosscut by a network of fine heterodromous cracks infilled with light-colored dolosparite (molar-tooth structure). In the middle part of the section of this association, one can observe rare traces of local erosion and horizons of intraformational

¹ The nomenclature of carbonate rocks is adopted from (Gary *et al.*, 1972).

breccia. The upper section consists of an intercalation of pelitomorphic dolomites and fine-grained doloarenites with numerous horizons of intraformational conglobreccia and separate interlayers of grainstones. Clastic layers have a heterodromous cross-lamination and contain up to 10% silty-sandy siliciclastic admixture in the northern and central sections. The cross-lamination is mainly oriented along the southwestern direction. In the central Golyi Yar and the northern Turukhansk block, these sediments incorporate rare and small (0.5–2.0 m) bioherms of *Baicalia rara*. The thickness of the association increases from 40 m in the northern Turukhansk block to 90 m in the southern Golyi Yar block and likely does not exceed 40–50 m in the northern Golyi Yar. These variations primarily occur at the expense of the finest part of the section.

The fine-grained and pelitomorphic sediments of the lower horizons were formed below the storm wave base as a result of the transportation of the major component of these sediments, i.e., the silt-size clastic carbonate fraction, by suspension flows. Massive dolomicrosparites likely represent the pelitic part of this fraction. The middle horizons of this association with breccia and erosion traces were accumulated near the storm wave base, while the upper horizons were formed near the fairweather wave base, as evidenced by the appearance of conglobreccia, grainstones, and cross-laminated doloarenites. The sediment flow was oriented in the southwestern direction (Fig. 2). Thus, the lower section of the second association terminates the deepening trend initiated by the first association, whereas the middle and upper sections reflect the successive shallowing of the basin.

(3) The **parallel and wavy-laminated dolomite association** corresponds to member 3 (thickness 20–25 m). In the southern Golyi Yar block, it is composed of the monotonous, light gray dolosparites with a vague but fine parallel lamination. In the northern zones, the association is split into two parts. The lower part contains subordinate varieties of dolosparites with an irregular wavy lamination that likely includes elements of microbial laminations. These rocks incorporate rare and small stratiform stromatolite domes, a few nodular buildups, and local erosional traces. They are marked by structures that can be qualified as a result of the fixation and cementation of migrating ripples by cyanobacterial mats. The upper part of this association in the northern zones is characterized by the prevalence of wavy-laminated dolosparites over parallel-laminated varieties and the appearance of polygonal desiccation cracks and dissolution breccia, which are confined to erosion surfaces, particularly in the central and northern zones. Such breccia make up indistinctly delimited and irregular bodies penetrating 15–20 cm down the erosion surface. In the central Turukhansk block, wavy-laminated dolomites incorporate the early diagenetic cherty concretions with abundant remains of filamentous cyanobacteria. The top of the association

includes small (1–3 mm) slit-type cavities resulting from the leaching of gypsum crystals.

The major unit of this association, represented by dolosparites with a continuous parallel microlamination, was likely formed at the expense of fine-clastic carbonate silts, whereas the wavy-laminated dolomites were formed from sediments associated with the microbial activity. This inference follows from both the lamination pattern of these rocks and the abundance of cyanobacterial mat remains in the dolomite-replacing cherts. On the whole, the third association reflects the lateral differentiation of depositional environments and the subsequent shallowing of the basin. In the southern zone, all types of sediments of this association were accumulated in stillwater conditions of the upper subtidal zone. In the northern zones, such conditions were retained only during the accumulation of the lower units of this association, while the upper units represent sediments of the intertidal and partly supratidal (?) environments. In these environments, the longest desiccation periods emphasized by the development of karsts were noted in the northern zone (Kamennaya River).

(4) The **fine-grained, stromatolitic, and clastic dolomite association** composes a thick (more than 330 m) sequence corresponding to member 4 of the lower subformation in the southern Golyi Yar block. It is subdivided into three facies of alternating small packages and separate beds.

The predominant **fine-grained dolomite facies** is mainly composed of dark gray dolosiltites and dololutes with a fine (0.5–1.0 mm), parallel, often graded bedding and admixture of sand-size carbonate particles. The rocks form up to 50-m-thick packages of monolithic beds that are usually penetrated by a network of diverse (in shape and size) cracks infilled with white dolosparite (molar-tooth structure). The cracks are subdivided into two types. Type 1 cracks, which are relatively fine, deform the lamination of host rocks to a variable extent and are commonly subnormal to the bedding surface. Type 2 cracks, which are larger and sigmoid, do not distort the lamination and stretch along or intersect the bedding at 40°–60°; their clusters divide the beds into separate fragments and often produce breccia, in which the random-oriented fragments, 1–20 cm in size, are cemented by light-colored dolosparite. The cement content increases from 5 in solitary crack clusters to 20% in breccia. The breccia make up irregular and large (up to 20 m) bodies that crosscut the boundaries of different-facies packages. The subordinate unit of this facies is represented by up to 20-cm-thick beds of syngenetic conglobreccia and flakestone horizons confined to the upper section.

The **doloarenite facies** is encountered as solitary beds and up to 5-m-thick packages of usually well-sorted sediments with parallel graded or cross (and cross-wavy) lamination. Clastic grains are represented by well-rounded isometric fragments of lithoclasts and

scraps of stromatolite laminae with dissemination of oolites and oolite aggregates. Large grains occasionally include deformed (crushed) or corroded varieties (Fig. 3c) that likely represent the strongly altered oolites. Doloarenites and fine-grained dolomites usually compose up to 10–30-m-thick cycles, in which the fragment size increases upward the section. In the lower 20-m-thick section of the fourth association along the Sukhaya Tunguska River, rocks of this facies are enriched in the rounded gravel–pebble carbonate material to a variable extent, and are characterized by the abundance of cross-wavy lamination. The overlying 2-m-thick package of cavernous, slightly ferruginous dolomites includes intraclastite layers, fine (0.2–0.5 cm) clay interlayers, and polygonal desiccation cracks, up to 5 cm deep.

The **clastic-stromatolite facies** is subdivided into four packages (2–20 m thick) dominated by stromatolites that commonly make up low-relief biostromes, subordinate isolated groups of buildups, and rare (up to 2-m-high) bioherms (Serebryakov, 1975). Stromatolites are represented by columnar branching *Baicalia lacera*, less common *B. rara*, and columnar stratiform individuals that do not differ from the above taxa in microstructure. Clastic units of this facies form biostrome-separating beds (0.2–2 m), and infill the interbioherm (and partly intercolumnar) space. The rocks are represented by dark doloarenites and unsorted breccia composed of stromaclasts and rarer lithoclasts in the sand–gravel matrix. Occasionally, the matrix contains dissemination of silt–sand-sized siliciclastic grains.

The fourth association, except for the cavernous package therein, was accumulated in the lower subtidal environment. Fine-grained dolomite facies likely represents an environment located below and near the storm wave base. Intraclastite horizons, which are rare in this facies, were related to the storm wave activity. Judging from the frequent traces of host layer condensation, type 1 fine cracks appeared at early stages of diagenesis, while type 2 cracks and associated breccia were possibly generated by the postformational compaction during the late zonal dolomitization. Large (up to 3 m) septarian nodules in the fine-grained dolomite facies in lower reaches of the Sukhaya Tunguska River were related to the early diagenetic local cementation of muds in relatively shallow-water environments, while the deeper sediments were characterized by a dispersed and irregular cementation during the burial. The doloarenite and clastic-stromatolite facies, which were mainly formed during constant or frequent wave activity, were characterized by an early, usually syngenetic lithification. Only cavernous dolomites represent the intertidal environment. Thus, the fourth association reflects the lower subtidal open-sea environments established as a result of rapid flooding and intense subsidence of the southern zone previously occupied by a shallowing basin.

(5) The **brecciated and laminated dolomite–lime-stone association**, which is mainly confined to member 4 of the central Turukhansk block, is as much as 140 m thick along the Nizhnyaya Tunguska River. In the northern part of the block (Kamennaya and Nadporozhnaya rivers), the association is significantly replaced by dark bituminous dolomite and is preserved only as a small (20–25 m) dolomite wedge at the base of member 4. In the Golyi Yar block, this association is absent: it gives way to the bituminous dolomite in the south and probably wedges out in the north (Fig. 2). The fifth association is separated from subjacent rocks by a sharp erosional boundary and subdivided into two facial types.

The predominant type 1 facies is represented by the dark gray fine-grained carbonates (dolosiltites, calcisiltites, and lutites) that contain series of contiguous, stratiform, and occasionally subvertical bodies of postdiagenetic breccia consisting of host carbonate fragments of different shapes and sizes (from a few millimeters to 20 cm). Such fragments are oriented at different angles to the bedding and submerged into the uniform microsparitic matrix (Fig. 3d). The fine-grained carbonates have a distinct thin lamination, which is parallel in dololutites and calcilutites, but striated, irregular-wavy (amplitude 0.1–1.0 cm), and lensoid in dososiltites and calcisiltites (Fig. 4a). In some lenses, one can observe the second-order cross microlamination. The finest sediments have a molar-tooth structure. The fine-grained carbonates make up 2–10-m-thick cycles with erosional boundaries and grading of the pelite–silty variety upsections into silty sediments. The top parts of the cycles are decorated with numerous erosion traces, desiccation cracks (Fig. 3e), and postdiagenetic breccia that make up stratiform bodies and lenses connected by subvertical, commonly wedge-shaped bodies. The breccia are confined to hummocky erosion surfaces near the top parts of the cycles and penetrate down to 20–40 cm in the northern sections and to 2.5–3 m in the central sections. Hence, the breccia represent products of the selective dissolution of carbonate rocks during their subaerial exposure.

The subordinate type 2 facies is represented by dark graded dososiltites and calcisiltites with parallel lamination, as well as calciarenites and doloarenites with horizontal or cross-trough lamination. Grainstone interlayers in the sequence are confined to minor erosion surfaces. The rocks usually make up separate thin (0.5–2.5 m) layers. However, near the base of the association along the Nizhnyaya Tunguska River, the layers converge into a 23-m-thick package, in which the grain size increases upward the section. The package is underlain by an 18-m-thick layer of type 1 facies rocks, in which the amount and degree of subaerial exposition traces also grows upward the section. The same pattern is observed in the 25-m-thick package (type 1 facies) representing the fifth association in the Kamennaya River area.

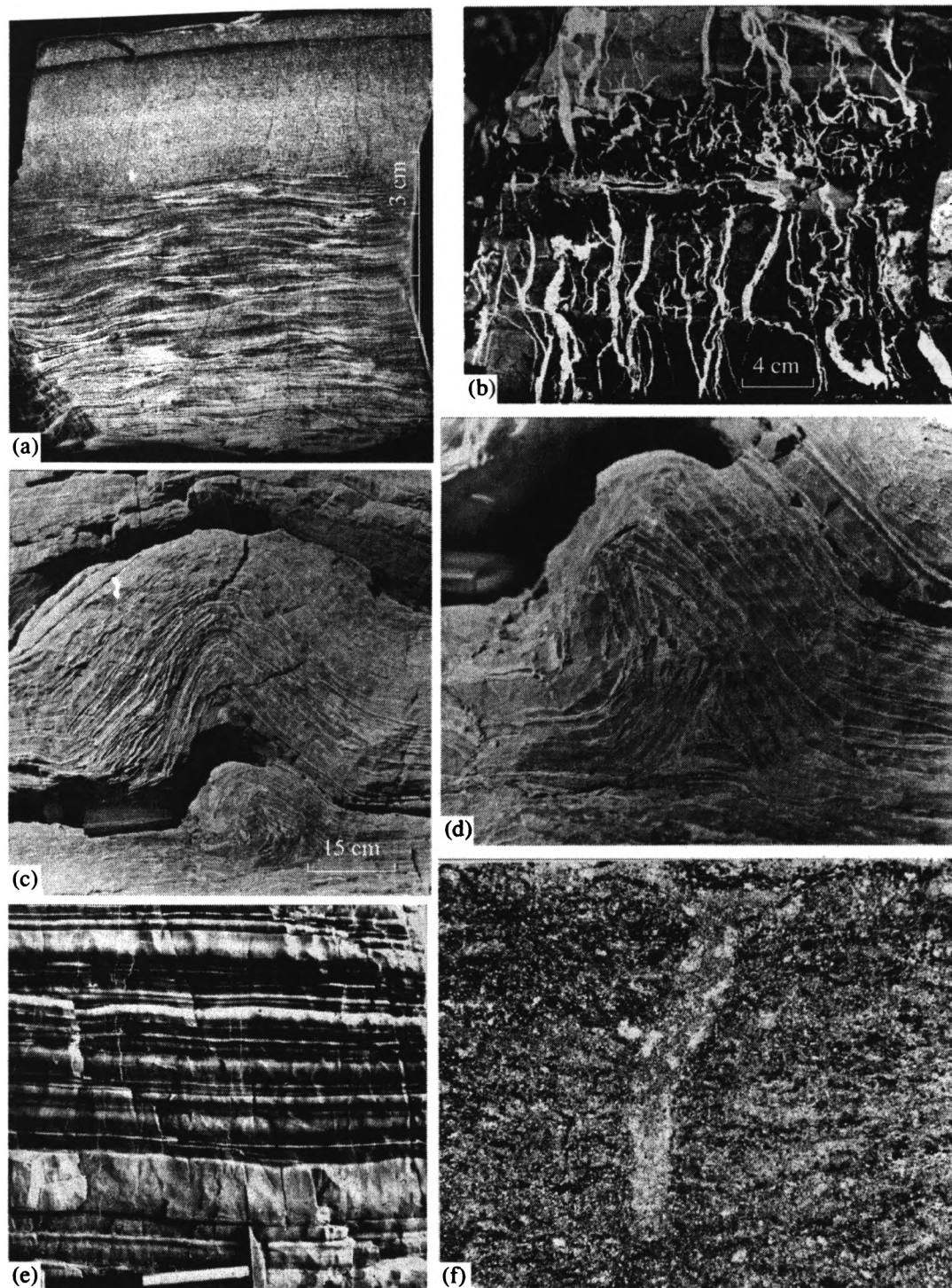


Fig. 4. Some facial features of sediments of the lower and upper subformations of the Burovaya Formation. (a) Lensoid lamination in calcisiltites of the brecciated and laminated dolomite–limestone association, Nizhnyaya Tunguska River below the Strel'nye mountains, polished section; (b) syneresis cracks (molar-tooth structure) in the dark-colored dolomite association, Kamennaya River, photograph of outcrop; slump fold in the fine-clastic pelitomorphous limestone facies (perireefal association), Nizhnyaya Tunguska River below the Strel'nye mountains, photograph of outcrop; (c) general view of fold, (d) fold core; (e) parallel lamination in the bituminous and pelitomorphous limestone–dolomite facies of the perireefal association, Kamennaya River, photograph of outcrop; (f) disturbances of microlamination in limestones of the clayey striated-laminated limestone–dolomite association, Nizhnyaya Tunguska River below the Strel'nye mountains, thin section (the arrow shows the sediment interface).

Thus, this association was likely formed in two types of shallow-water environments: (1) the shallow stillwater (lagoonal?) sectors of the upper subtidal and intertidal zones with the frequent and prolonged periods of subaerial expositions followed by karst formation (type 1 facies), and (2) the relatively deeper subtidal zones characterized by the migration and accumulation of granular carbonate sediments (type 2 facies).

(6) The **dark-colored molar-tooth dolomite association** is developed in the northern Turukhansk block (Kamennaya and Nadporozhnaya rivers). Here, this association is registered as a 250–270-m-thick sequence that incorporates the entire member 4, except the lowermost 25-m-thick unit. The major component is represented by uniform, dark gray to black, bituminous crystalline dolomites with a parallel lamination emphasized by a dispersion pattern of organic matter. The rocks are crosscut by a dense (up to 40 vol %) network of subvertical syneresis cracks infilled with white dolosparite (Fig. 4b). The cracks are restricted to individual beds and pinch out toward the bottom and top of beds. The subordinate light-colored dolomites are characterized by striated and irregular-wavy (possibly, microbial) lamination and rare molar-tooth structures. The rocks make up small (4–10 m) cycles with sharp boundaries. Upward the cycles, the relative amount of wavy-laminated dolomites increases at the expense of the horizontal-laminated variety. Additionally, erosional surfaces and breccia interlayers appear near the top of each cycle. Nonrounded and unsorted fragments of light-colored dolomites are accumulated in depressions of some erosional surfaces with a relief amplitude up to 10–15 cm. Hence, we can suggest that dolomites of the sixth association originated from clastic pelite-silt sediments accumulated in the upper subtidal zone under stillwater environments periodically interrupted by short-term drainings that promoted the surficial dissolution and partial erosion of sediments.

FACIAL COMPLEXES OF THE UPPER SUBFORMATION

As stated above, the upper subformation of the Burovaya Formation, preserved only in the central and northern zones of the Turukhansk block, is subdivided into two facial complexes: the dominating thick (320–550 m) reefal complex and the terminating subordinate (up to 130 m) cover complex.

Reefal Complex

The reefal complex includes reefal and perireefal associations. The reefal association overlies different facial associations of member 4 of the lower subformation and is separated from the latter by an erosional boundary with a relief amplitude up to 1.5 m (e.g., the Nizhnyaya Tunguska River area below the Strel'nye mountains). The perireefal association rims the reefal association and locally conformably overlies the reef

periphery. The contact of the perireefal association with the lower subformation is unexposed in sections studied.

(7) The **reefal association** represents a system of diverse (in morphology) large stromatolite buildups along with subordinate clastic and pelitomorph carbonate sediments (major light gray dolomite and rare limestone). In the northern Turukhansk block, it is most developed and makes up the entire section (e.g., more than 550 m in the Bolotnaya River section), almost the entire section of the upper subformation (more than 450 m in the Malaya Shorikha River section). In other sections, this association makes up different (in thickness and stratigraphic position) horizons and wedges among the perireefal sediments (Fig. 2). This association is subdivided into three facies.

The **bioherm-biostrome facies** is most developed in upper reaches of the Malaya Shorikha River where it is more than 270 m thick and makes up almost the entire visible section of the seventh association. The facies also stretches into adjacent zones of the Turukhansk block as a 30–50-m-thick horizon at the base of the subformation and forms wedges and units of different sizes, including large ones, within overlying rocks in the Turukhansk block (Bolotnaya River and Maiskii Creek) and Golyi Yar block (Nizhnyaya Tunguska River and upper reaches of the Miroedikha River). The facies is composed of a combination of stromatolite bioherms and biostromes with rare clastic carbonates. Bioherms include both isolated and laterally connected varieties (3–10-m in thickness and 5 to 50–60 m in length). The synoptic relief varies from dekameters in small bioherms to 3.0–3.5 m in large ones. Biostromes (thickness 1 to 4–5 m) overlie certain bioherm levels, or alternate with intraclastites in separate packages, up to 12–15 m in thickness. The lower horizons of bioherms are usually composed of columnar branching *Baicalia* and rare *Tungussia* that are commonly underlain by a thin (10–30 cm) stratiform crust above the erosional surface of subjacent rocks. In the upper horizons of bioherms, the columnar-stratiform varieties predominate while the stratiform varieties prevail in the buildup roofs. Biostromes are composed of predominant stratiform (including the tisaget-type) and columnar-stratiform buildups. The columnar varieties are represented by *Baicalia* and *Tungussia*. Additionally, *Conophyton miloradovici* Raab. has been found in the 1.5-m-thick bed in the Golyi Yar section along the Nizhnyaya Tunguska River.

All of the above-mentioned stromatolitic morphotypes in the Turukhansk block do not differ much in microstructure from the typical *Baicalia lacera* discovered at the bioherm-biostrome facies base in the Nizhnyaya Tunguska River section located below the Strel'nye mountains. However, in the shallower-water section of the facies revealed in the Golyi Yar block, two additional microstructures are observed. In the majority buildups or in certain fragments, one can observe microstructures related to the trapping and

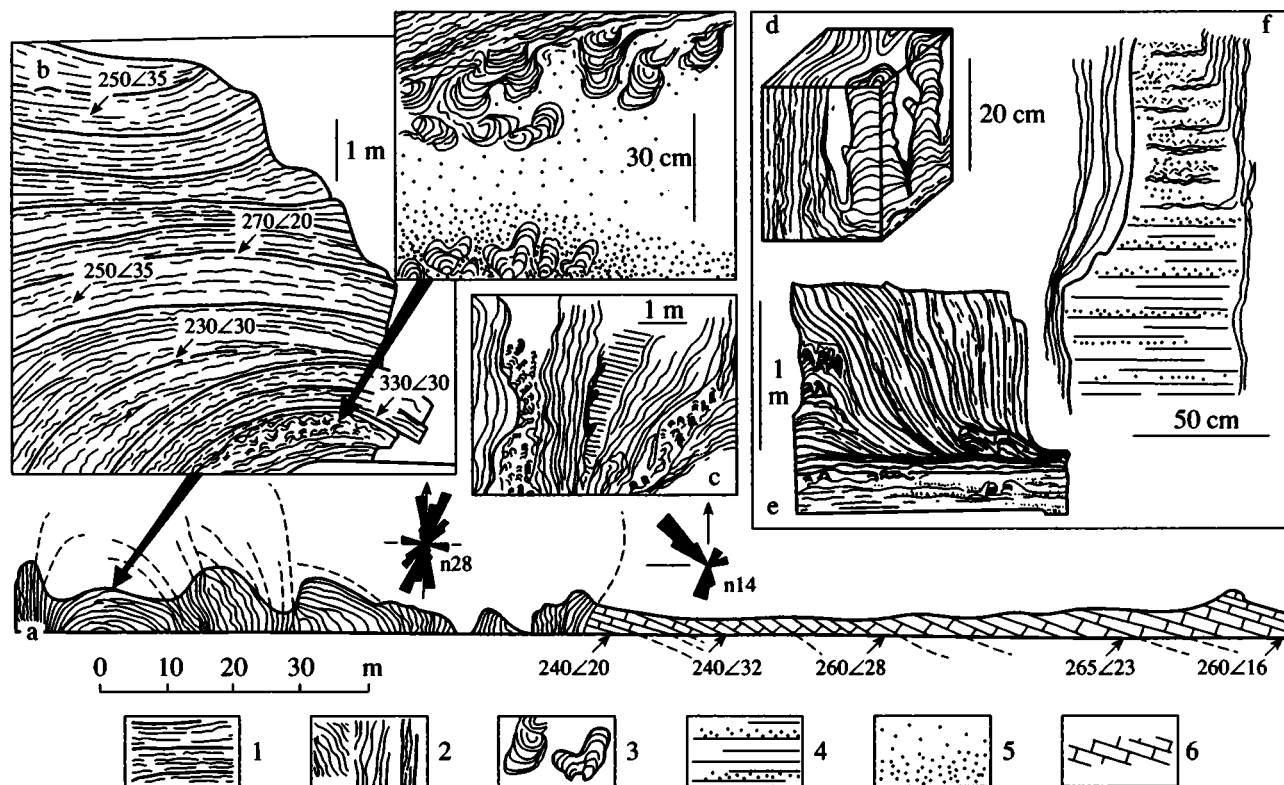


Fig. 5. Closeups of the large dome-facies (reefal association) structure. (a) Profile of a large reefal structure and host deposits along the Maiskii Creek; (b) slit-shaped cavity between stratiform stromatolites in the crest area of dome; (c, f) vertical wedges within the stromatolite dome infilled with nonstromatolitic sediments: (c) relatively wide wedge, (f) narrow wedge revealing relationships of the lamination within the wedge and the host stromatolitic dolomites; (d) columnar stromatolites located on the bench of a subvertical limb of the dome; (e) relationships between horizontal and vertical stromatolite laminae within the dome. (1–3) Stromatolites: (1) stratiform with subhorizontal laminae, (2) stratiform with subvertical laminae, (3) columnar; (4–5) nonstromatolitic intradome sediments: (4) laminated and fine-grained, (5) massive; (6) fine-grained sediments in intradome spaces. Rose diagrams of the strike of subvertical limbs of domes ($n = 28$) and the growth of subvertical stromatolite buildups ($n = 14$). Numerical pairs indicate the bedding elements.

binding of clastic carbonate particles. These microstructures differ from that of *B. rara* by lesser dimension, higher sorting, and the closer packing of particles. Additionally, a specific, relatively coarse, irregular-striated microstructure of *Conophyton miloradovici*, which is also developed in some tissaget buildups, is also observed here.

Clastic rocks of this facies are represented by two varieties. The horizontal- and cross-laminated variety (dolocarenites and calcarenites with abundant stromatoclasts) infills the interbioherm spaces, or makes up minor interlayers and lenses within bioherms. The second variety (intraclastites) forms 1–2-m-thick interlayers within biostromes.

The **large dome facies**, which is only developed in the northern Turukhansk block and constitutes a major part of the reefal association along the Bolotnaya River and Maiskii Creek, is registered in the form of two large bodies (100 and 250–270 m, respectively) separated by the bioherm–biostrome facies. The dome facies penetrates into the northern zones as a small wedge. Along

the Bolotnaya River, one can observe that this facies is separated from the subjacent bioherm–biostrome facies by a sharp erosional boundary.

The dome facies is represented by submeridionally elongated domes, which are a few tens of meters high and several hundreds of meters long (along strike) structures. In the transverse section, they have narrow (20–25 m) gentle crests and steep (60°–90°) flanks that are tens and hundreds of meters wide (Fig. 5a). The major part (80–85%) of these buildups are composed of stratiform stromatolites with accretion almost completely oriented in the subhorizontal direction. Therefore, the dome limbs are wide and steep. The exposed synoptic relief of these buildups is as much as 20–25 m. The rare components of this facies are represented by small, sometimes columnar branching stromatolites that are randomly clustered on swells or benches of the subvertical dome limbs. This morphotype is also occasionally observed near the crest zone in small slit-shaped cavities between stratiform buildups (Fig. 5b). In such cavities, infilled with the younger, homoge-

neous, fine-grained carbonate sediment, the buildups grow both upward and downward.

A specific element of domes is represented by the downward tapering wedges (apparent depth up to 3 m and width up to 2.0–2.5 m) infilled with more or less crystalline nonstromatolitic dolomites. These dolomites were formed at the expense of fine-clastic carbonate muds that locally contain nonrounded fragments of stromatolite laminae and elements of microbial lamination. The relationship between wedge bedding and stromatolite lamination shows that the wedges were generally filled with sediments after the formation of the vertical walls of domes and sometimes simultaneously with the accretion of domes (Fig. 5f).

The large (up to 200 m across) spaces between domes are filled with the horizontal-laminated dolosparite containing relics of the fine-grained, laminated clastic carbonate sediments and rare microbial laminae. In the upper part of this facies along the Maiskii Creek, the rocks incorporate breccia, in which the nonrounded fragments (up to 10 m across) are composed of stromatolitic rocks from surrounding domes.

Stromatolites of these domes have a common *Baicalia lacera* microstructure and contain abundant calcified cyanobacterial filaments. The filaments usually occur along the plane of stromatolite laminae and locally at an angle to the laminae, or they are interwaved, as in some *Baicalia* and *Tungussia* from bioherm–biostrome facies of the Burovaya Formation and its analogues in the Igarka Uplift (Knoll and Semikhov, 1998, Figs. 2–4). The presence of the aforesaid filaments (fossilized sheaths of cyanobacteria *Lyngbya*, *Phormidium*, and *Plectonema*) emphasizes that these stromatolites were primarily formed as a result of the active precipitation of carbonate material by cyanobacterial mats (*op. cit.*). Locally, along the Bol'shaya Shorikha River, above the Nadporozhnaya River mouth, stromatolites developed near the top of the Burovaya Formation contain small (millimeter-scale) lenses or patches of tiny (less than 0.2 mm) clastic carbonate particles.

The **parallel-laminated dolomite and biostrome facies** is observed as a 20–70-m-thick unit at the top of the reefal association in the Malaya Shorikha River section and northern zones of the Turukhansk block. It is composed of the predominant yellowish gray and cherry red crystalline dolomites that, judging from relic structures, were formed from the pelite–silt-size clastic laminated and sometimes microbial sediments. These rocks include small (up to 1 m thick) biostromes of stratiform stromatolites *Stratifera* and *Thyssagetacea* with the typical *Baicalia lacera* microstructure.

The three facies described above for the reefal association were formed in different environments. The bioherm–biostrome facies represents a wide range of the relatively shallow-water environments. The repeated replacement of bioherms by biostromes, changes of the morphology of stromatolites and compositional varia-

tions of associated clastic carbonates in this association are an evidence of frequent transitions from the conditions of fairweather wave activity to shallower-water, mainly stillwater conditions with episodic destructions of the cemented seafloor sediments. Such shallowing trends are characteristic of the majority of stromatolitic sediments in the Proterozoic carbonate platforms (Grotzinger, 1989; Southgate, 1989; Sami and James, 1994). The origination of stillwater conditions in these environments was likely related to the active growth of stromatolite buildups and the isolation of some sectors in the basin. Thus, on the whole, the bioherm–biostrome facies reflects short-term oscillations of the sea-level against the background of its general rise.

The large dome facies was accumulated in deeper-water environments. The lack of clastic sediments or any sign of graded structures in sediments, which infill the interdome depressions, suggests that the summits of the largest domes were located below the effective storm wave base. Since the synoptic relief of buildups exceeded 20–25 m, the depth of the dome facies formation could be several tens of meters. In such environments, the horizontal accretion of domes predominated over the vertical component, and the interdome depressions were filled with laminated and fine-grained background sediments bounded by rare microbial mats. Megabreccia horizons in these sediments represent periodic gravitational sediments accumulated near the foothills of growing domes. However, the parallel-laminated dolomite and biostrome facies, which includes the low-relief stromatolite buildups, clastic muds, and microbial sediments, were likely accumulated in protected stillwater lagoons that were formed in the reef zone at terminal phases of its development.

The spatial relationship between the three facies of the reefal association suggests that the reef massif was characterized by a lateral zonality during almost its entire evolution period. Its southern and eastern zones were dominated by the variable (in hydrodynamic activity), relatively shallow-water environments that occasionally penetrated into the northern zones (bioherm–biostrome facies). However, on the whole, these zones were characterized by the prevalence of deep-water conditions (large dome facies). At the final stage of the reefal association, its entire domain was occupied by lagoonal conditions (parallel-laminated dolomite and biostrome facies).

(8) The **perireefal association** surrounds reefal buildups from the south, east, and north. In the Turukhansk block sections along the Kamennaya and Nizhnyaya Tunguska rivers, this association is most complete and dominates in the upper subformation (thickness 280 and 220 m, respectively). Fragments of its sections are encountered along the Miroedikha and Nadporozhnaya rivers in the Turukhansk block and along the Nizhnyaya Tunguska and Miroedikha rivers in the northern Golyi Yar block (Fig. 2). This association consists of the dark gray and black, often bitumi-

nous, dolomites and limestones that can be subdivided into four facies.

The **bituminous pelitomorph limestone-dolomite facies** is mainly developed in the Turukhansk block as a major part of the perireefal association in the Nizhnyaya Tunguska River area (thickness up to 160 m) and makes up separate 30–40-m-thick units along the Kamennaya River and is partly exposed along the Miroedikha River. Within the Golyi Yar block, it is encountered in upper reaches of the Miroedikha River and forms a small unit along the Nizhnyaya Tunguska River. This facies is composed of dark-colored, homogeneous, fine-grained limestones and crystalline dolomites. The parallel-laminated limestones, enriched in dispersed organic detritus (especially, near the top of the association), are found as small continuous beds (Fig. 4e) with very fine (0.2–0.6 mm), pelite-silty graded structures. The rocks are cut by large (up to 50 cm long and 10 cm wide) subvertical fissures filled with paler microsparite. Dolomites, which retain only relics of graded structures, contain epigenetic compaction breccia and sigmoid cracks analogous to those described above.

The **fine-clastic and pelitomorph limestone facies**, which gradually replaces the underlying limestone and dolomite facies, terminates the perireefal association along the southern framing of the reef massif within the Turukhansk block. Along the Nizhnyaya Tunguska River, it is represented by a dark gray 80-m-thick unit of parallel-laminated, fine-graded (0.5–1.5 mm) calcisiltites and calcilutites with rare syneresis cracks. Among the clastic grains (micritic particles) scraps of thin films of organic matter are disseminated. Traces of soft sediment deformation, which is typical of this facies (specifically, its upper section), are manifested in both the microlevel (microlamination distortion) and the macrolevel (slump folds). In the upper section, numerous folds with acute-angle overturned hinges encompass the 40–50-cm-thick packages. The upper layers of these packages were soft during the slump. The lower layers were partly cemented and brecciated (Figs. 4c, 4d). The sediments were mainly displaced in a northwest direction (Fig. 2).

The **boulder facies** is encountered as separate beds and 15–20-m-thick packages within the bituminous pelitomorph limestone-dolomite facies along the Kamennaya River in the Turukhansk block and along the Nizhnyaya Tunguska River in the Golyi Yar block. It is composed of dark gray, laminated and massive, fine-grained dolomites with up to 2-m-thick beds of nonlaminated wackestones and separate fragments of stromatolitic limestones and dolomites, from decimeters to 8–10 m in size. In the Kamennaya River area, the appearance of these fragments is followed by the soft sediment deformation and mixing of the host fine-grained sediments. In the Nizhnyaya Tunguska area, the clastic material includes diverse-oriented, sometimes overturned bioherms of *Baicalia rara*, up to 2.0–2.5 m

across. After the dislocation, some of these fragments were overgrown with a new generation of columnar-stratiform stromatolites.

The **stromatolite facies** is only developed in the Kamennaya River basin in the form of two 20–25-m-thick packages among the bituminous pelitomorph limestone-dolomite facies. It is represented by up to 2-m-thick stromatolite biostromes and rare bioherms (up to 4–5 m across) that are separated by dark gray, fine-grained laminated dolomites. Stromatolites are generally represented by the stratiform varieties (*Stratifera* and *Thyssagetacea*) that make up biostromes of different dimensions. The rarer columnar forms constitute low-relief separated bioherms (small *Baicalia*) and, in one case, a chain of contiguous bioherms, up to 3.0–3.5 m high, in which the deep-water *Conophyton* (*C. cf. metula* Kir.) is vertically replaced by shallower-water *Jacutophyton* and rarer *Baicalia*. The poor preservation of microstructures hampers a more precise determination of these stromatolites.

The foregoing data suggest that the perireefal association was accumulated below or near the storm wave base. The southern foothill of the reef massif was the site of accumulation of the bituminous pelitomorph limestone-dolomite and the fine-clastic and pelitomorph limestone facies that represent the distal deep-water sediments of the flat, slightly inclined perireefal plains with a mixed (background and event) sedimentation of very fine carbonate muds. On the east and north of the massif, these facies were intersected by the proximal and possibly shallower-water deposits of the boulder and the stromatolite facies that were accumulated in the foothill and lower zones of the reef slope near the storm wave base. The facies distribution and thickness variations of the reefal and perireefal associations indicate that the southern slope of the reef massif occupied a stable position in the Nizhnyaya Tunguska and Malaya Shorikha interfluvial zone during a major period of the late Burovaya time. The slope was surrounded in the south by an intensely subsiding zone of the accumulation of deep-water carbonate sediments (bituminous pelitomorph limestone-dolomite facies). Simultaneously, the massif's eastern and northern margins, which were occupied by the above-mentioned relatively shallower-water facies, were characterized by periodic lateral expansions of reefal sediments to the fine-grained mud zone and the subsequent accumulation of gravitational boulder facies.

Cover Complex

The cover complex makes up a thickness-variable body that overlies the perireefal association and the periphery of the reefal association without any visible unconformity. In the central zone of the reef massif, in the Malaya Shorikha and Nadporozhnaya interfluvial area, the cover complex pinches out. Here, the reef is unconformably overlain by shales and sandstones of

the basal unit of the Shorikha Formation. The complex is subdivided into two associations.

(9) The **clayey striated-laminated limestone-dolomite association** is developed in the south and north of the reef massif within the Turukhansk block and penetrates into the central Golyi Yar block in upper reaches of the Miroedikha River. Along the Nizhnyaya Tunguska River in the Turukhansk block, this association is represented by a 66-m-thick sequence of continuous beds of dark gray, slightly clayey, fine-grained limestones (5–30 cm) separated by 0.5–2.0-cm-thick interlayers of gray marls and shales. Limestones have a very thin (0.1–1.0 mm), slightly wavy-striated lamination often emphasized by the distribution of fine-dispersed organic matter. Locally, these rocks include vertical, very thin (0.2–0.5 mm) and short (up to 3 mm) aggregates differing from the surrounding rocks by the prevalence of a paler carbonate cement (Fig. 4f). In rare patches of such aggregates (up to 5–6 mm across), the lamination is completely deteriorated. These microstructures, resembling the bioturbation traces, were likely originated in the unconsolidated sediment as a result of rapid dehydration followed by the nonuniform condensation and early cementation. The association is represented by dolomites in northern outcroppings on the opposite side of the stromatolite reef (the Nadporozhnaya River mouth area) and by clay-rich varieties with a reduced number of lamination disturbance traces in the southernmost zones (upper reaches of the Miroedikha River).

The ninth association comprises the major fine-grained clayey-carbonate and the subordinate clayey sediments periodically bounded by microbial mats. The influence of microbial mats in the past is suggested by the characteristic striated lamination of rocks and the presence of organic detritus. The sediments were accumulated in stillwater environments that excluded any storm impact upon the basin floor. The comparison of various sections in this association indicates that the basin deepened toward the south.

(10) The **variegated shales association** is only developed on the south of the reef massif within the Turukhansk block. Along the Nizhnyaya Tunguska River, it is 58–60 m thick and represented by dark gray to greenish gray and brick-red shales with a massive structure or vague thin (0.1–0.5 mm) parallel lamination that is sometimes emphasized by the color distribution. Shales contain a minor (<5%) admixture of the silt-sized siliciclastic material and small clayey pellets along with fine dispersion of iron hydroxides.

This association is very similar (in accumulation environments) to the subjacent association, except for a more intense input of clayey material into the basin. On the whole, the cover complex reflects the process of paleobasin filling and the establishment of stillwater environments in the reef periphery. The shallowing, which should have inevitably accompanied the filling, did not leave any visible traces in the cover complex,

probably because all sediments were accumulated in stillwater conditions. Meanwhile, the reef's central zone, where the complex pinches out, was perhaps partly exposed but the massif roof was not appreciably eroded.

EVOLUTION OF THE PALEOBASIN AND FACIAL SYSTEMS OF THE BUROVAYA FORMATION

The foregoing data on the composition, distribution, and formation conditions of different facial units, as well as the paleoflow direction makes it possible to trace the variation of paleoenvironments in time and space, reconstruct the general structure of the Burovaya Formation, and identify the main event boundaries. We took into consideration the fact that the Burovaya Formation sections in the Golyi Yar and Turukhansk blocks are tectonically convergent. The convergence value is not known for certain; however, it is likely equal to tens of kilometers, because the displacement amplitude of the lowest (in structure) Golyi Yar block, based on geophysical data of N.N. Dashkevich, amounts to 40–50 km.

The Burovaya Formation sediments were accumulated within a large carbonate platform characterized by significant structural rearrangements. The most prominent event divides the platform evolution into two stages corresponding to the lower and upper subformations. Based on the formation environments and the geometry of associations and facies, each stage can be subdivided into phases (Fig. 6).

The **first stage** is subdivided into three phases. Phases 1 and 2, represented by two (transgressive and highstand tract) facial systems, were characterized by the predominance of more or less laterally homogeneous environments. Phase 3, which is represented by a lowstand system tract, was characterized by the basin's facial heterogeneity owing to a differential intensity of the subsidence of separate zones.

Phase 1 is noted by a gradual flooding of the shallow-water carbonate platform of the late Derevnaya time (Petrov and Veis, 1995). The beginning of flooding is registered over the entire area on the basis of the replacement of stillwater lagoonal sediments in the upper package of the Derevnaya Formation by sediments of the open-sea subtidal zones (the clastic-bioherm association of member 1 of the Burovaya Formation). Further development of the transgressive system mirrors the replacement of sediments of the upper subtidal zone by sediments of the agitated, lower subtidal zone (the first and second facies of the clastic-bioherm association, respectively) and the subsequent pervasive accumulation of sediments below the storm wave base (lower horizons of the pelitomorph and granular dolomite association). The slowly subsiding shallow-water (upper subtidal and intertidal) zone was retained only in the northeastern part of the region (the northern sections of the Golyi Yar block) at the beginning of

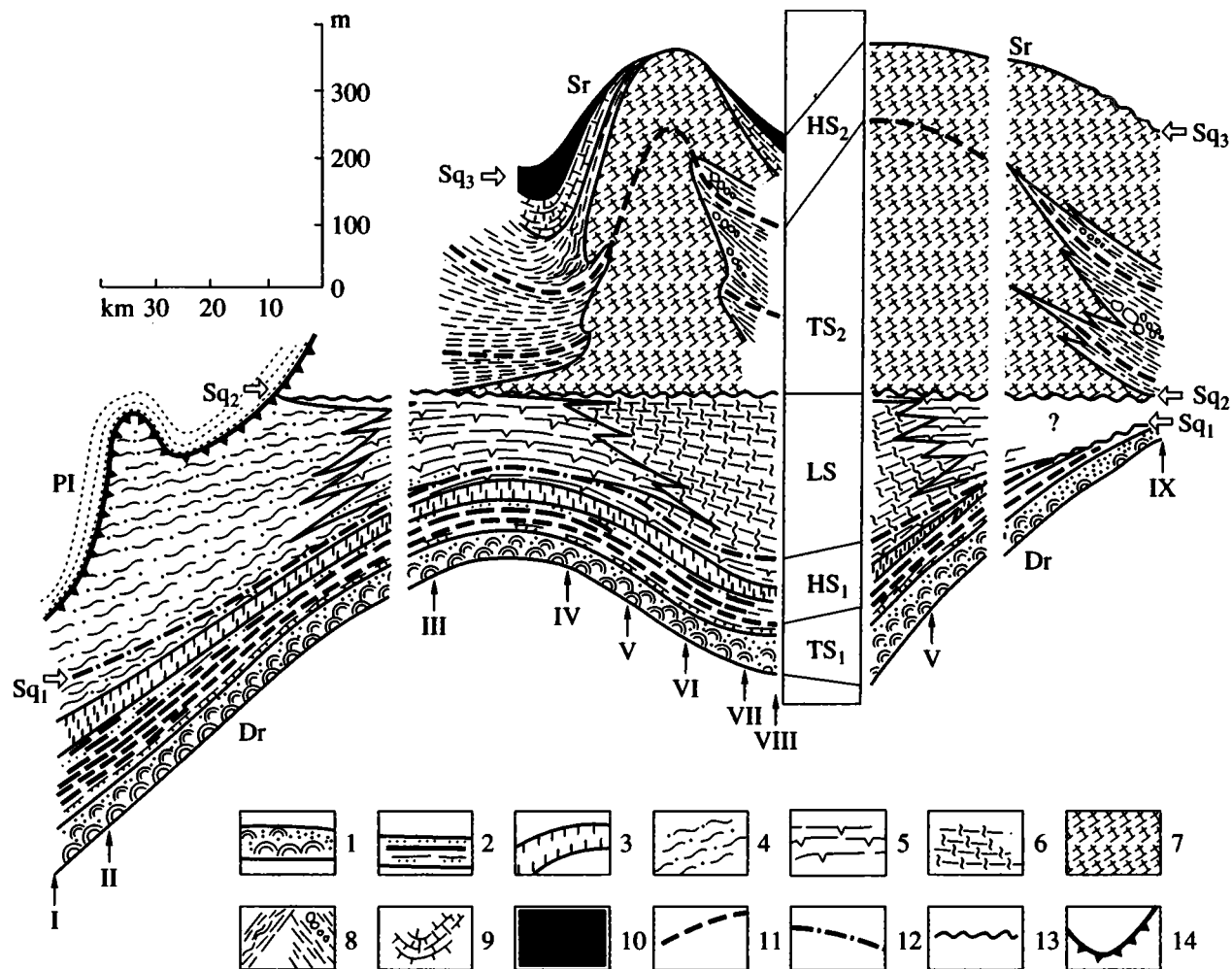


Fig. 6. Sequence stratigraphy and facial structure of the Burovaya Formation. Facial associations: (1) clastic-bioherm, (2) pelitomorphic and granular dolomite, (3) parallel- and wavy-laminated dolomite, (4) fine-grained, stromatolitic, and clastic dolomite, (5) brecciated and laminated dolomite-limestone, (6) dark-colored molar-tooth dolomite, (7) reefal, (8) perireefal, (9) clayey striated-laminated limestone-dolomite, (10) variegated shales; major event boundaries: (11) maximum sealevel stand, (12) minimum sealevel stand, (13) major erosional unconformity in the Burovaya Formation, (14) regional pre-Vendian unconformity. Indices: (Sq) sequence boundaries; facial systems of sediments: (TS) transgressive, (HS) highstand, (LS) lowstand; formations: (Dr) Derevnya, (Sr) Shorikha, (Pl) Platonovskaya. (I–IX) Sections studied (see Fig. 1).

phase 1. On the whole, judging from variations of the composition and thickness and directions of paleoflows, phase 1 sediments were accumulated within a stable shelf zone that was steeply subsiding in the west-south-west direction (here and henceforth, the directions are given in the present-day coordinates). The termination of the phase 1 history of the early Burovaya basin is determined by the flooding maximum surface. It is registered on the basis of the replacement of lower horizons of the pelitomorphic and granular dolomite association accumulated below the storm wave base by its middle horizons that reflect the transition to agitated environments.

Phase 2 is represented by sediments located between the flooding maximum surface and the overlying shallowing maximum surface. In various zones of the region, the shallowing maximum surface is regis-

tered by the replacement of different sediments. In the southern open marine sections, it separates the above-described cavernous, 2-m-thick, dolomite package, which reflects intertidal environments and terminates the shallowing trend, from the overlying clastic-stromatolite facies (sediments of the lower subtidal agitated zone). In the central zone, the shallowing maximum surface passes near the base of the brecciated and laminated dolomite-limestone association. It separates the shallowest-water sediments (the basal 18-m-thick package) of type 1 of this association from the overlying type 2 sediments accumulated in relatively deeper-water subtidal zones. In the northern sections, the shallowing maximum coincides with the interface between the phase 1 karstified sediments of the brecciated and laminated dolomite-limestone association and the overlying, dark-colored, molar-tooth dolomite associa-

tion that represents stillwater environments of the upper subtidal zone characterized by the short-term periodic subaerial exposures.

Phase 2 was mainly characterized by the basin's gradual shallowing that commenced under the conditions of high sealevel stand. This feature was most pronounced in the northern zone (northern sections of the Turukhansk block and the Golyi Yar block, in particular) with reduced sections of the shallowest-water facies that is replaced southward by thicker sections of the deeper-water facies. This type of the distribution of sedimentation environments and rock thickness suggests two inferences concerning the phase 2 (early Burovaya stage) evolution. First, an intense subsidence was developed in the southern zone, and the carbonate platform was distinctly inclined toward the southwest. Second, the beginning of phase 2 was marked by a transition from the shelf structure to the platformal ramp structure, and the transition period did not coincide with the maximum transgression. It is worth mentioning that such a transition is not typical for the majority of carbonate platforms evolving in the ramp-shelf direction (Grotzinger, 1989; Burchette and Wright, 1992).

The facial zonality of phase 2 rocks was governed by the above-mentioned zone of relatively intense subsidence in the south. Thus, the shallowing maximum corresponded to the boundary between two facial associations only in the northern shallowest-water zone, whereas it separated certain unit within associations in the southern zones. These facts indicate that the boundaries of the highstand system tract were eustatic.

Phase 3 is represented by sediments deposited between the shallowing maximum surface and the erosional surface at the top of the lower subformation. These sediments correspond to the lowstand system tract, because stillwater environments were retained in a major part of the region, except the southern zones, during the formation of these sediments. The analysis of the composition and thickness of facial associations shows that phase 3 was characterized by a progressive structural differentiation of the region, i.e., the intensification of subsidence in the southern zone, the origination of a sublittoral synsedimentary uplift in the central zone, and the development of a gentle subsidence zone on the north of the uplift, a part of which was reported by Dragunov (1959).

The intensely subsiding southern zone is noted by the formation of a more than 350-m-thick sequence of the open sea, fine-grained, stromatolitic, and clastic dolomite association. The sequence represents a shallowing succession, in which the lower section is dominated by deepest-water sediments of the lower subformation. The northerly synsedimentary uplift, which is separated from the southern zone by a sharp bend of the basin floor, is ascertained by the appearance of the 140–150-m-thick, shallowest-water sediments of the brecciated and laminated dolomite–limestone association and

their pinch-out (or at least sharp reduction) in the northern Golyi Yar block. Hence, one can conclude that the uplift encompassed a wide zone in the central part of the region, rose toward the east, and stretched for several tens of kilometers along the strike (the latter estimate follows from the probable value of tectonic convergence of the aforesaid blocks). Meanwhile, the northern subsidence zone, which rimmed the relatively gentle slope of the uplift, was characterized by the accumulation of a 250–280-m-thick, black-colored, molar-tooth dolomite association, representing the upper subtidal conditions interrupted by short-term subaerial exposures. This zone likely corresponded to the distal zone of a partly isolated intraplatformal basin.

Hence, at the final phase 3 of the early Burovaya basin evolution, the structural rearrangement of the carbonate platform resulted in a transition from the homoclinal ramp to the distal-subsided ramp. The phase 3 culmination was noted by the draining of the entire territory or major part of the northern zone and the erosion of older sediments.

Remarkably, during the whole first stage, stromatolites avoided both shallowest-water and deepest-water environments. A major part of stromatolites (clastic-bioherm association) was confined to transgressive tracts in the shelf-related subtidal environments with a variable hydrodynamic regime. They disappeared toward the shallow-water zones (e.g., northern Golyi Yar sections) and during the sealevel rise (late phase 1 to early phase 2). The open-sea shelf environments were favorable for the development of a field (belt?) of small stromatolite reefs with a synoptic relief as high as 3.0–3.5 m. Such reefs are common for Proterozoic environments ranging from shallow-water shelf conditions to relatively deep-water ones (Serebryakov, 1975; Geldsetzer *et al.*, 1988; Grotzinger, 1989; Narbonne and James, 1996; Petrov and Semikhatov, 1997; and others).

Thus, the whole first stage of the Burovaya basin evolution was characterized by a progressive lateral differentiation of facies and thicknesses of sediments. The differentiation reached its maximum at the final phase. Based on the above-described data, the first stage sediments could be considered a single sequence, although its thickness (up to 520 m) is not typical for similar divisions of carbonate platforms (Read *et al.*, 1991; Burchette and Wright, 1992). Taking into consideration the high event significance of shallowing, which terminated the phase 2 evolution of the early Burovaya basin, we are inclined to divide the lower subformation into two stratigraphic sequences separated by the maximum shallowing surface (Fig. 6).

The **second stage**, represented by the upper subformation, is distinguished from the first stage by the predomination of deeper-water and distal environments and the formation of a large stromatolite reef that was surrounded and partly overlapped by fine-grained laminated sediments. The conformable sedimentary suc-

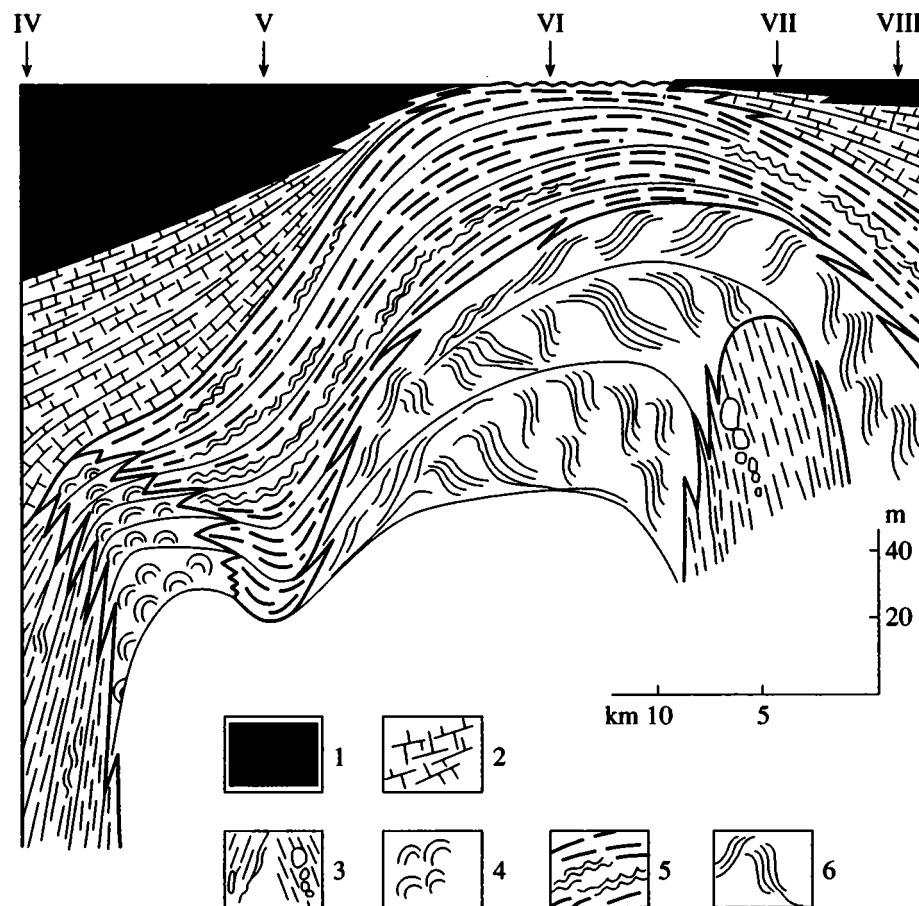


Fig. 7. Facial reconstruction of the upper part of reefal and cover complexes. Cover complex associations: (1) variegated shale, (2) clayey striated-laminated limestone-dolomite; (3–6) facial units of the reefal complex: (3) perireefal association, (4–6) facies of the reefal association: (4) bioherm-biostrome, (5) parallel-laminated dolomite and biostrome, (6) large dome.

cession is confined to the zone between the main event boundary in the Burovaya Formation (bottom of the upper subformation) and the erosional unconformity at the bottom of the Shorikha Formation. The second stage is subdivided into two phases: phase 1 reflects the transgressive facial system, while phase 2 represents the highstand system tract.

Phase 1 was characterized by a rapid flooding of the erosional surface at the top of different facial associations of the lower subformation and the accumulation of the lower reefal complex under the conditions of a significant lateral heterogeneity of environments. The heterogeneity was displayed in localization patterns of not only reefal and perireefal associations but also facies within each of the association.

In the western zone (within the Turukhansk block), the first wave of transgression at the beginning of phase 1 was noted by the most extensive development of stromatolites in the late Burovaya history (Figs. 2, 6). They formed a system of size-variable but usually large bioherms with the synoptic relief as high as 3–4 m. In the eastern zone (Golyi Yar block sections), this time interval was marked by the accumulation of the perireefal

association. However, the presence of stromatolitic rock boulders here (Nizhnyaya Tunguska River) suggests the proximity of the reef slope to this zone.

Progressive transgression was responsible for two essential events in the basin's history. First, the stromatolite domain in the Turukhansk block sections was reduced owing to the lateral expansion of both the deepest-water facies of the perireefal association from the southern, deeper-water side of the area (Nizhnyaya Tunguska River) and the shallower-water sediments of the same association from the northern side (Kamenaya River). Second, the relic stromatolite domain (basins of the Malaya Shorikha and Bolotnaya rivers) was overgrown with a large stromatolitic reef massif, and a lateral zonality that appeared in the morphology of buildups of the massif. Precisely during this time interval, small bioherms of relatively shallow-water bioherm-biostrome facies were developed along the massif's southern periphery adjoining the deep-water zone of accumulation of the bituminous pelitomorph limestone-dolomite facies of the perireefal association. Meanwhile, the deep-water and considerably larger reefs (large dome facies) started to form in the massif's

inner zone. Toward the north (Kamennaya River), the large dome facies was replaced by the perireefal deeper-water association represented by thin deposits of all three facies, including the boulder facies. In the eastern and southeastern zones of the basin (Golyi Yar sections), the perireefal association (the boulder plus the bituminous and pelitomorph limestone-dolomite association) was the main representative of this episode. Small (20–30 m) wedges of the bioherm-biostrome facies (reefal association), which were penetrated into this zone (Nizhnyaya Tunguska and Miroedikha rivers) only at the end of phase 1, reflect the sporadic expansion of the reef massif toward the east and southeast.

The phase 1 culmination is registered by the major flooding maximum surface. On the south of the massif, in the bituminous and pelitomorph limestone-dolomite facies, like in other similar successions (Loutit *et al.*, 1988), the aforesaid surface passes inside the finest and condensed sediments (bituminous and pelitomorph limestone-dolomite facies) with the highest concentration of organic matter. Within the reef, this surface coincides with the contrast erosional boundary separating the different (in formation depth) bioherm-biostrome facies from the large dome facies. On the north of the massif, the flooding maximum surface passes along the level where the boulder facies is replaced by the deeper-water bituminous and pelitomorph limestone-dolomite facies. In the Golyi Yar block, the flooding maximum surface is not so evident. Here, it likely separates the bituminous and pelitomorph limestone-dolomite facies from the subjacent shallowest-water units of the bioherm-biostrome facies. In such a restricted transgressive system tract, in certain sections of the perireefal association, one can observe elevated contents of organic matter in the finest carbonate sediments, suggesting a local maximum of the high sea-level stand, traces of which are lost in the reef massif.

Phase 2 is represented by sediments of the upper reefal complex and cover complex that are restricted by a flooding maximum surface at the bottom and a transgressive boundary (at the base of the Shorikha Formation) at the top. These sediments correspond to the highstand system tract and represent the shallowing succession. The beginning of phase 2 was characterized by a lateral expansion of the reef massif and a further differentiation of the sedimentation environment and subsidence intensity in various zones of the basin. The phase 2 termination was noted by a collapse of the reef system, the gradual filling of the relic relief by carbonate-clayey sediments of the cover complex, and the considerable leveling of environments over the entire area (Fig. 7).

Based on the Turukhansk block sections, at the beginning of phase 2, the reef massif in the western zone evolved within spatial limits of the previous phase, but the phase 1 lateral zonality was more prominent. The deepest-water facies of the reefal association

(large dome facies) occupied the whole inner zone of the massif and was characterized by greater thicknesses, relative to the shallower-water bioherm-biostrome facies that continued to dominate over the massif's southern periphery. Appreciably thinner deep-water deposits of the fine-clastic and pelitomorph limestone facies of the perireefal association were accumulated to the south of the massif. Sediments of the aforesaid facies and boulder facies were deposited on the northern side.

The Nizhnyaya Tunguska River section located in the Golyi Yar block shows that this time interval was noted by a significant eastward expansion of the massif. Taking into consideration the tectonic convergence of blocks, the expansion can be estimated at several tens of kilometers. The reefal association units here probably composed the marginal, relatively shallow-water zone of the reefal complex with abundant biostromes (*Baicalia* and *Tungussia*) and subordinate deep-water buildups (*Conophyton* and *Thyssagetacea*) at certain levels. The reef massif expansion was likely accompanied by the intensification of its accretion and the growth of the synoptic relief. This conclusion is based on the appearance of avalanche boulder rocks within the reef and the extensive development of gravitational processes on slopes of its framing.

In most of the sections studied, the final periods of the reef formation (Fig. 7) were noted by the accumulation of thickness-variable lagoonal sediments (parallel-laminated dolomite and biostrome facies of the reefal association). Only along the massif's northern periphery (Kamennaya and Bol'shaya Shorikha rivers in the Nadporozhnaya River mouth area), in the roof of the Burovaya Formation, the deep-water large reefal domes, which compose up to 50-m-thick packages, appear above perireefal sediments. This suggests a mosaic pattern of environments in the area and the massif's sporadic interventions into new areas at the final period of its existence.

At the end of the Burovaya time, the above-described events were followed by the deposition of still-water sediments of the cover complex. These sediments are rapidly reduced in thickness toward the central zone of the massif and pinch out in the present-day section. However, one cannot rule out that, during the final periods of the late Burovaya history, this zone incorporated shallow-water lagoons filled with thin sediments of the parallel-laminated dolomite and biostrome facies that were eroded during the pre-Shorikha episodic hiatus. These sediments were likely accumulated mostly in the massif's inner zone protected by the marginal stromatolite belt (Fig. 7).

The late Burovaya history of the Turukhansk block was terminated by a drastic sealevel drop and draining. Consequently, the basal sandy-shale unit of the Shorikha Formation overlapped not only various facial associations but also different horizons of the Burovaya Formation. Nevertheless, the thinning zone of the cover

complex at the reef summit lacks any karst formations or other distinct signs of exposition that are typical for several stromatolite reefs subject to a prolonged subaerial exposure in the latest period of the reef development (Geldsetzer *et al.*, 1988; Grotzinger, 1989; Narbonne and James, 1996). The cover complex was likely formed in a short time interval, during which a geomorphologically prominent but only partly exposed uplift composed of lithified reefal sediments existed in the pinch out zone of the aforesaid complex.

Thus, the late Burovaya stage of basin's evolution represented the period of birth, development, and extinction of a large stromatolitic reef massif. Simultaneously, a significant lateral differentiation of environments and subsidence intensity was observed in different zones of the basin. The differentiation was markedly leveled at the final phase of the reef development and during the deposition of the cover complex, in particular.

On the south, the most intensely subsided zone of the late Burovaya basin represented a site of deepest-water accumulation, partly uncompensated sediments of the perireefal association and deposition of the younger, relatively thick lagoonal succession of the cover complex (Figs. 2, 6). At the same time, at a distance of a mere 5–6 km on the north, a major period of the early Burovaya stage was characterized by the development of an outer belt of the stromatolite reef composed of the shallowest-water units of the reefal association (the bioherm–biostrome facies and the subsequent parallel-laminated dolomite and biostrome facies) that were replaced by thin deposits of the cover complex only at the end of the early Burovaya stage. The depth gradient from the southern deep-water zone to the reef periphery was likely as much as hundreds of meters and reflected the presence of a sharp tectonic bend in the basin floor relief. The bend, located in the Nizhnyaya Tunguska and Malaya Shorikha interfluvial area, was appreciably displaced northward from a similar bend that existed in the early Burovaya basin.

The uplifted edge of the bend was the site where the outer open-sea (but relatively shallow-water) belt of the reef complex was located. On the north, this belt was generally replaced by deeper-water and thicker buildups of the reef's inner zone. Such a zonal structure of the massif owing to tectonic factors existed during a prolonged period of the second stage. Only at the end of this stage, the homogeneous (in composition) but variable (in thickness) lagoonal sediments crowning the reef complex were deposited over the entire reef. The northern edge of the reef on the left bank of the Kamennaya River is not known for certain. However, it is highly probable that the edge represented a narrow zone of interfingering of the large dome facies with deeper-water (but thinner) sediments of the perireefal association represented here by all of the three facies (Figs. 2, 6). Thus, the reef width reaches 15–20 km in the Turukhansk block sections. The reef's western edge is

located beyond the Turukhansk block, whereas the eastern edge is ascertained in the northern zone of the Golyi Yar block on the basis of the presence of boulder facies rocks (perireefal association) and certain wedges of reefal association in the lower section of the upper subformation. At the top of the upper subformation, the reef's edge is identified by the prevalence of shallow-water sediments in the thick reefal association.

The dynamics of facial zones within the reef massif is not known for certain. However, the available data suggest that the sealevel drop was followed by the northward migration of the shallow-water lagoonal environments from the rear zone of the massif's outer belt. The latter represented a geomorphologically distinct and stable barrier that was retained up to the latest period of the massif existence (Fig. 7).

Based on the foregoing data, we can infer that the second stage sediments were deposited within a distal-subsided (toward the southwest) ramp that incorporated the sublatitudinal large stromatolitic reef massif. The massif, 15–20 km wide and not less than several tens of kilometers long (along the strike), can be attributed to the previously described (Grotzinger, 1989) reef of the barrier ramp type.

The available data indicates that the upper subformation of the Burovaya Formation unites sediments of two facial systems and constitutes a single sequence. Its lower boundary is represented by a transgressive surface that overlaps the partially eroded sediments of different facial associations of the lower subformation, while the upper boundary is represented by the surface of the pre-Shorikha draining and local shallow erosion (Figs. 6, 7).

CONCLUSION

The Burovaya Formation illustrates an example of the direct correlation between the origination and growth intensity of stromatolites, on the one hand, and the carbonate platform structure and the sealevel dynamics, on the other. Like the counterparts in several Proterozoic successions (James, 1984; Geldsetzer *et al.*, 1988; Grotzinger, 1986a, 1986b, 1989), the Burovaya stromatolite buildups, which were at a stage of maximum development at the beginning of the sealevel rise, preferred the open-sea zones of carbonate platforms. During the later phases of transgression and high sealevel stand, in particular, the buildups persistently avoided intraplatformal shallow-water environments where the fine-clastic carbonate sediments were mainly deposited.

The above-described open-sea zones were sites of the formation of stromatolite reefs of different dimensions. In contrast to several other large-scale Precambrian stromatolite buildups (Donaldson, 1976; Khabarov, 1985, 1990; Grotzinger, 1986a, 1986b; Geldsetzer *et al.*, 1988; Khabarov and Tanygin, 1991; Narbonne and James, 1996), the largest Burovaya reefs

from the upper subformation neither subsided below the effective stromatolite accretion zone during the sea-level rise nor were exposed to the intense erosion zone during the sealevel drop. Such a scenario suggests the existence of a certain mechanism that regulated the balance between the intensity of vertical accretion of reefs, their erosion, and variations of the relative sealevel.

Modern genetic models (Grotzinger and Knoll, 1995 and references therein) make it possible to assume that the major regulators of the aforesaid balance includes the hydrological factor, i.e., the mixing of surface waters, which are supersaturated with calcium carbonate, with the deep anoxic waters with an elevated alkali metal reserve and the consequent precipitation of calcium carbonate. If this assumption is correct, the tectonic factor (i.e., the basin floor structure) governed the temporal rather than the spatial disposition of reefs. The termination of the reef massif development in the deeper-water zone could be induced by the origination of a new barrier reef system that served as the site for carbonate material discharge. The discharge drastically reduced the carbonate productivity of the inner zones of platforms. Consequently, the biochemogenic carbonate precipitation, related to metabolism of the cyanobacterial stromatolite-building communities, was dominated here by the deposition of clastic carbonate materials.

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Isotopic Evidences of Epigenetic Transformations and the Problem of the Age of Riphean Rocks in the Uchur–Maya Region, Eastern Siberia

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Abstract—Riphean rocks of the Uchur–Maya region underwent strong post-sedimentation transformations from deep epigenesis to metagenesis. These alterations obliterated K–Ar and Rb–Sr signatures of fine-grained clastic material provenance. An isotopic age of epigenetic transformations of rocks is lower than a possible sedimentation age by hundreds of millions of years. It is assumed that the isotope system reflects the time when rocks sequentially pass through certain depth and temperature boundaries, and where the rate of mineral transformations sharply increases. The carbon and oxygen isotopic composition of carbonate rocks is, on the whole, rather homogeneous across the section, indicating that the isotopic composition of carbonates is more conservative during their secondary changes. A positive anomaly of $\delta^{13}\text{C}$, which was previously observed at approximately the same stratigraphic level in the Yudoma–Maya trough (Podkovyrov and Vinogradov, 1996), is clearly defined in the lower Lakhanda Formation (Upper Riphean). This anomaly apparently can be used as a stratigraphic datum mark.

INTRODUCTION

Within the vast Uchur–Maya region of Eastern Siberia, the Riphean rocks exposed over a wide area are very thick and have a varied facial composition. Because of its stratigraphic completeness, an abundance of paleontological findings, and a distinct relationship with the underlying pre-Riphean and overlying Vendian–Lower Cambrian sequences, the Uchur–Maya Riphean rocks substantially supplement the southern Ural type section and is considered as its hypostratotype (Semikhatov and Serebryakov, 1983). However, researchers estimates vary in volume and position for the boundaries of these subdivisions (Komar, 1990; Krylov, 1985; Semikhatov and Serebryakov, 1983; Semikhatov *et al.*, 1991; Shenfil', 1991, and others), despite a highly appreciated geology of this region and repeatedly substantiated possibilities for distinguishing basic Riphean subdivisions. Due to such discrepancies, basic component division of the integral sedimentary sequences of the Uchur–Maya Riphean into reliable and disputable units is very demonstrative for the Precambrian stratigraphy and remains typical of other regions as well. It is characteristic that age reliability and nonreliability of these units are almost never reviewed with the use of new data. The set of parameters usually applied for the substantiation of rock age remains, on the whole, constant and well-known to the adherents of different viewpoints. This set is rather restricted and includes information about the position of specific sequences in a composite section of the region, lithologic features of rocks, cyclic rhythmical-

ity of sedimentation, association of phytoliths and microfossils, as well as isotopic geochronology and, to a lesser degree, chemostratigraphy.

Each member of this set has certain methodical restrictions in substantiation stratigraphic position of rocks. The applied methods are based on a study of variability caused by fundamentally different natural processes. Therefore, their independent use in interregional correlations often gives incompatible results. Moreover, it is true that researchers very rarely use specific (biostratigraphic, isotopic, etc.) methods for correlation of the Riphean successions (including the Uchur–Maya with its southern Ural stratotype). More frequently, the causes promoting correlation are obscure and require convincing evidence based on an advanced complex study. However, the combination of data received from such diverse methods and justified by the necessity of integral (multidisciplinary) correlation of the Precambrian sections, does not necessarily result in helpful discussion, especially when one could impartially assess the data obtained, try to relate them to the data available, and critically misinterpret the information potential of the independent methods applied. It becomes further evident that, at present, one should hardly assume a position which would elaborate on integral but intrinsically contradictory complex schemes of age division and correlation of Riphean successions. A common-sense solution would be to preliminarily elucidate the factual potential of each method and then accumulate and analyze new data. We suppose that this paper takes a step in this direction.

GEOLOGICAL CHARACTERISTICS OF RIPHEAN ROCKS IN THE UCHUR-MAYA REGION

Riphean rocks are distributed in two main structural-facial zones of the region: Uchur-Maya plate (southeastern margin of the Siberian Platform) and Yudoma-Maya trough (southwestern segment of the Verkhoyansk-Kolyma fold system). In the Uchur-Maya zone, gently dipping Riphean sequences fill two large depressions in the western (Uchur) and eastern (Maya) parts of the plate, they are exposed at the slopes of the Omnya uplift of crystalline basement rocks where these depressions separate. In the meridionally extended Yudoma-Maya trough, the rocks considered are noticeably dislocated and exposed mainly at the flanks and cores of anticlinal structures (Fig. 1). The geological structure of the Riphean succession in this region is briefly described below on the basis of detailed work (Semikhatov and Serebryakov, 1983).

Five large transgressive-regressive rhythms or groups—Uchur, Aimchan, Kerpyl, Lakhanda, and Ui—are distinguished in the entire Riphean succession of the region. This section is complete only in the northern Yudoma-Maya trough, whereas it is represented by obviously inequal fragments in different parts of the Uchur-Maya plate. The Uchur depression is almost exclusively filled with rocks of the Uchur group. In the Maya depression, only the Kerpyl and Lakhanda groups are complete, whereas the underlying Aimchan and Ui rocks, crowning the Riphean succession, are very restricted in volume and distribution. The typical for the region spatial separation of the main components of the Riphean succession, gave many researchers reason to undertake long-term efforts in order to elaborate the stratigraphic scheme accepted at present. This scheme is displayed in Fig. 2. Furthermore, we shall concentrate our attention only on the Riphean successions of the Uchur-Maya plate.

The most common feature of the Uchur-Maya subplatform's Riphean succession is its cyclic structure. Most megacycles (groups) distinguished here have a similar structure: they are separated by erosion surfaces, begin with coarse-grained rocks (conglomerates and sandstones) and end with carbonate rocks.

The **Uchur Group** rocks immediately overlie the crystalline basement and Ulsan-Uyan volcanogenic molasses of the Lower Proterozoic. This group is divided into three formations totalling in thickness of about 1500 m. The lower Gonam Formation is represented mainly by conglomerates and sandstones. Further up the section, grains decrease in size, and claystones and siltstones appear in addition to sandstones. Dolomites interlayers are observed in certain sections of the lower Gonam Formation. The overlying Omakhta Formation is represented by a specific fine rhythmic alternation of terrigenous and carbonate rocks (sandstones, siltstones, claystones, and dolomites). Carbonate interlayers occupy about 35% of the entire thickness

of this formation. The Enna Formation crowning the Uchur Group is composed of several terrigenous and carbonate units. All three formations have commensurable maximum thicknesses.

In the supraplate sections, the **Aimchan Group** rocks are nowhere in direct contact with the underlying Uchur rocks. In the Yudoma-Maya trough, the Aimchan rocks overlie the Uchur rocks with distinct angular unconformity. The Aimchan Group (up to 1350 m) is composed of two formations: the terrigenous Talya and the terrigenous-carbonate Svetlin.

The next **Kerpyl Group** (1000–1200 m) includes three formations. The lower (Totta) formation is represented by sandstones, claystones, and siltstones. Its basal section, mainly composed of sandstones, is distinguished by certain researchers as an independent (Konder) subformation. The upper section with a larger amount of clay rocks is identified as the Omnya subformation. Two other (Malga and Tsipanda) formations are represented only by carbonate rocks. The Malga Formation is composed mostly of limestones, sometimes very bituminous, and the Tsipanda Formation is represented by dolomites. The indication of secondary dolomitization is observed in the Malga limestones; the Tsipanda dolomites contain breccias, apparently, of karst origin and numerous quartz-carbonate and quartz veinlets.

The overlying **Lakhanda Group** (500–600 m) is composed of two formations. The lower, Neryuen Formation is represented by carbonates and two units of fine-bedded claystones, and the upper, Ignikan Formation is composed only of carbonates.

The terrigenous **Ui Group** (300 m), completing the Riphean succession of the Uchur-Maya plate, also includes two formations: Kandyk and Ust'-Kirba. Both formations are represented by clastic rocks: sandstones, siltstones, and claystones. The main outcrops of the Ui rocks are located outside the considered supraplate section of the region, and only insignificant exposures of the Kandyk rocks are traced along the eastern margin of the Siberian Platform.

Among all the main subdivisions of the Riphean succession in Uchur-Maya, the Uchur Group is at present classified by all researchers as the Lower Riphean, the Aimchan Group belongs to the Middle Riphean, and the Ui and Ignikan formations of the Lakhanda Group are related to the Upper Riphean. The inclusion of the entire Kerpyl Group and the thicker lower Lakhanda Group (Neryuen Formation) to the Middle or Upper Riphean remains a disputable problem (Komar, 1990; Krylov, 1985; Semikhatov and Serebryakov, 1983; Semikhatov *et al.*, 1991; Shenfil', 1991; *et al.*).

K-Ar dating of glauconites was significant and maybe decisive among the complex of methods previously used for determining the age of the above subdivisions. Isotope glauconite datings were taken as the age of rock formation. Thus, the glauconite is dated as 1450–1520 Ma for the Gonam Formation of the Uchur

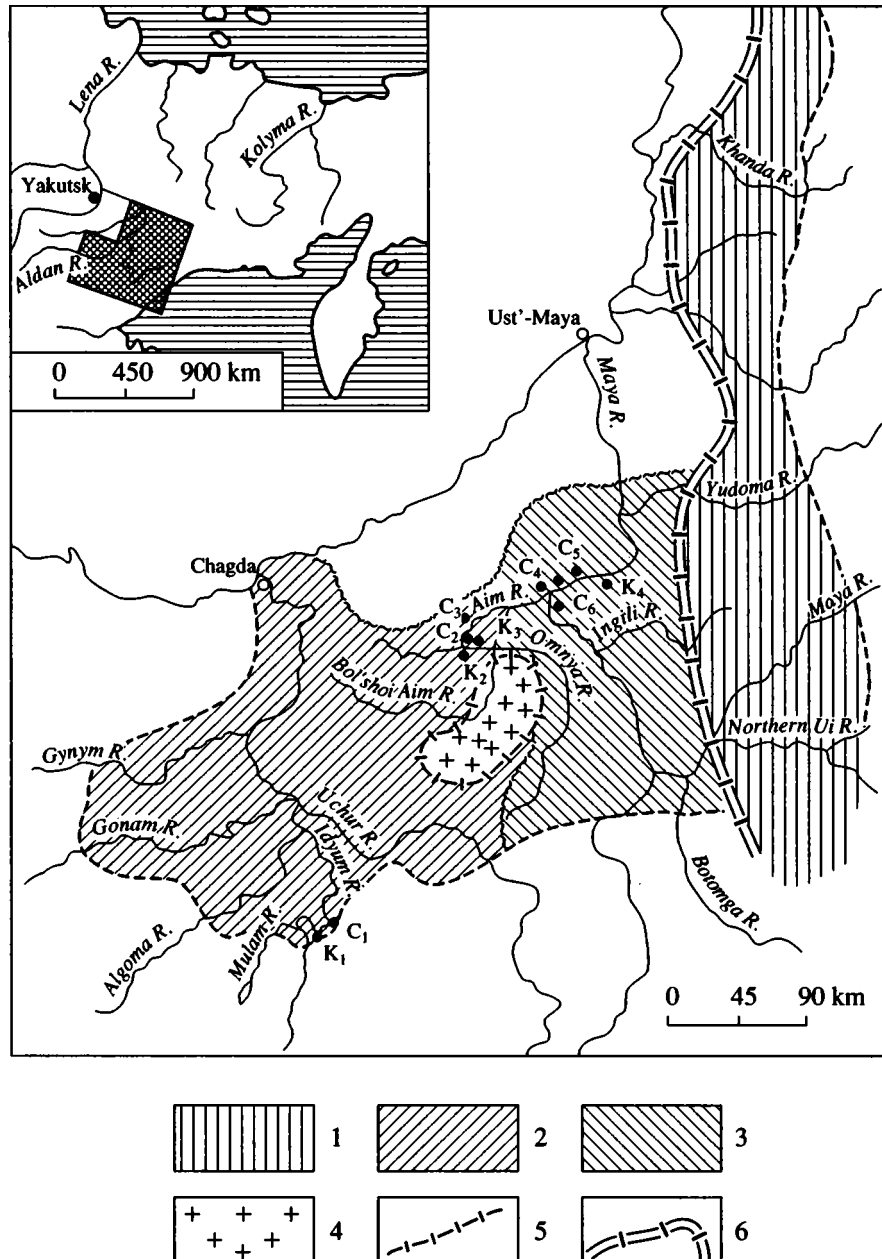


Fig. 1. Schematic map of the Uchur–Maya region and of sampling sites of (C) carbonate and (K) terrigenous–clay rocks. (1) Yudoma–Maya trough, (2) Uchur depression, (3) Maya depression, (4) Omnya uplift; boundaries between the main structural–facial zones: (5) Uchur–Maya plate and Yudoma–Maya trough, (6) Uchur–Maya plate and Omnya uplift. Sampling sites of carbonate rocks (stratigraphic position is shown in Fig. 2): (C₁) Idyum River, Sivaglikan Creek mouth area, (C₂) Bol'shoi Aim River, above the Malyi Aim River mouth, (C₃) Aim River, below the Malyi Aim River mouth, (C₄) the lower reaches of the Aim and Maya rivers, below the Aim River mouth, (C₅, C₆) Maya River, below the Neryuen Creek mouth. (K₁–K₄) sampling sites of terrigenous–clay rocks: (K₁) Idyum River, Sivaglikan Creek mouth area, (K₂, K₃) Bol'shoi Aim River, below the Omnya River, (K₄) Maya River, Bol'shoi Kandyk River mouth area.

Group, 1360 Ma for the Omakhta Formation of the same group, and 1210–1230 Ma for the Talyn Formation of the Aimchan Group (Semikhatov and Serebryakov, 1983). The present views on the age of the Kerpyl and thicker lower Lakhanda rocks are contradictory. Different researchers relate these rocks to the Middle or

Upper Riphean, or draw the Upper–Middle Riphean boundary between both groups. Such a wide range of opinions is first of all based on the analysis of contradictory isotope datings.

Four groups are distinguished among isotope datings of the Kerpyl and Lakhanda rocks (Semikhatov

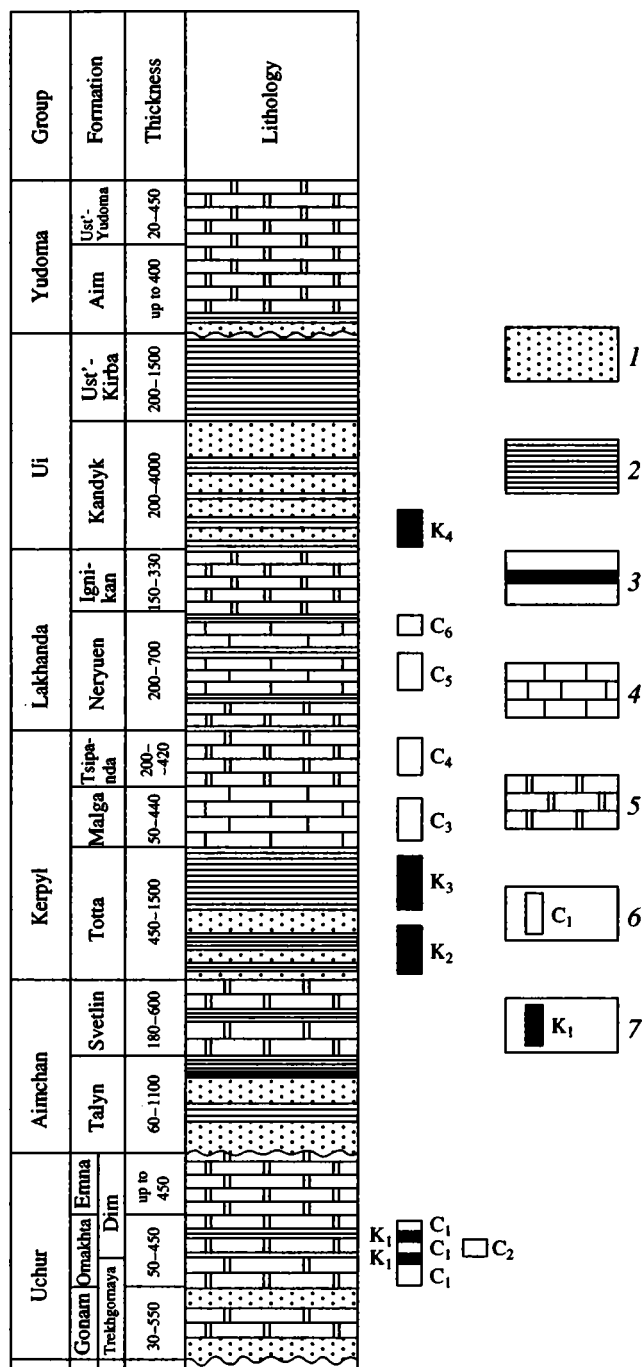


Fig. 2. The schematic lithologic-stratigraphic column of the Riphean rocks in the Uchur-Maya region and sampling sites of (C) carbonate and (K) terrigenous-clay rocks. Predominant lithologic varieties of rocks: (1) sandstones, (2) siltstones, (3) claystones, (4) limestones, (5) dolomites; sampling intervals of: (6) carbonate rocks, (7) terrigenous-clay rocks.

970 Ma for the Kerpyl Group and from 930 to 870 Ma for the Lakhandia rocks. Second, we have the Pb isochron datings of metamorphism of Tsipanda (980 Ma) and Ignikan (840 ± 40 Ma) dolomites (Gerling and Iskanderova, 1976). Third, we have two K-Ar datings of glauconite from probable analogs of the Kerpyl basal section revealed by the Mokui borehole near the Maya River mouth (1120 and 1115 Ma). Fourth, these are the K-Ar and Rb-Sr isochron datings of glauconitic and illitic hydromicas from natural outcrops of the same Kerpyl basal sections at the Bol'shoi Aim River (864 ± 4 Ma). The latter values, according to the researchers who obtain them, reflect regressive catagenesis rather than accumulation of host rocks. The generalization of the data listed has led certain researchers (Semikhatov *et al.*, 1989; and others) to the conclusion that the isotopic age of the Kerpyl Group falls within 1170-1000 Ma, and that of the Lakhandia Group is lower than 1000 Ma.

Such an interpretation of the isotopic geochronological information available is one of the main arguments for drawing the boundary between the Middle and Upper Riphean in the Uchur-Maya region along the Lakhandia bottom section. It is considered that this variant to greatly agrees with the Ural model of this boundary, where it approximates 1000 ± 50 Ma (Semikhatov *et al.*, 1991). The Sm-Nd dating of the dike (942 ± 18 Ma) intersecting the Ui rocks is in contradiction with the data accepted (Pavlov *et al.*, 1992).

PETROGRAPHIC FEATURES OF ROCKS

It is known that sand fractions are most informative about the degree and succession of epigenetic transformations of rocks. Unfortunately, sandstones were absent in the sample collection treated. Therefore, we had to deal with small (1-3 mm) lenses of fine-grained sandstones in the clay matrix of the rocks. To compare the alteration degree, we analyzed thin sections of the samples taken from the topmost (Kandyk) and lowermost (Omakhia) formations of the Riphean succession.

The Kandyk Formation is represented by the samples of varved or, sometimes, massive clayey siltstones. Laminated structures are predominant. Grading is observed in certain samples, which testifies to the pulsatory input of the portions of clastic material into the sedimentation basin. The rocks are composed of differently rounded quartz grains with a variable admixture of acid plagioclases, orthoclase, and microcline. Glauconite is present in rare grains.

Quartz is absolutely predominant, and feldspars vary from 0 to 17% (2-3% on average) in sand lenses and bands. Secondary conformal-sedimentation structures with virtually complete filling of original pore space with authigenic quartz are formed in sandstone bands and lenses. Authigenic rims appear on plagioclases. The refractive index of authigenic plagioclase is always lower than that of cores. The cores of clastic plagioclases are differently pelitized, but fresh rounded

and Serebryakov, 1983; Semikhatov *et al.*, 1991). First, these are K-Ar datings of glauconite from the rocks of both groups in the middle and lower reaches of the Aim and Maya rivers. They decrease in age from 1170 to

or subrounded grains of albite (possibly oligoclase) and microcline are also encountered.

A rock clay matrix is very consolidated and forms blocks with predominant subparallel orientation of particles. The initial mineral composition of clays is disputable. One can observe only post-sedimentation splitting of mica flakes, their distortion, coating of clastic grains, and subsequent transformation (aggradation) of particles into chlorite-muscovite packages.

The general rock structure corresponds to the stage of deep epigenesis. It is important that we point out the initially abundant pulverized organic matter. Initial thicknesses of sediments were considerably decreased, apparently, due to consolidation of the organic and clayey parts of rocks and burning out of the organic matter. At the same time, blocking by clayey and organic masses prevented the decomposition, conformation, and regeneration of the granular part of rocks. Conformal-regeneration structures appeared only in bands and lenses of well-sorted sands. Rare pockets of authigenic chlorite and muscovite with idiomorphic facets are encountered in the same places.

The Omakhta Formation is represented by mainly silty and sandy-silty marls with banded and micro-block structures.

The proportion between silicate and carbonate rock components is widely variable. A block structure is secondary and is formed during mechanical crushing of already lithified rock that has not yet undergone intense secondary changes. Bands and lenses are composed of arkose sands (Shutov, 1967). The presence of authigenic pyrite represented by globular microconcretions, sometimes transformed into pocket-like accumulations of dodecahedrons, is typical of all rocks.

The primary clastogene structure is clearly displayed in a present-day rock structure, but the indications of a new structure, caused by the appearance of authigenic orthoclases and muscovite, are prominent as well. Pelitomorphic carbonate remained only in lenses and bands of marls. In sand pockets, pore space is filled with inequigranular dolomite and authigenic orthoclase. The tendency toward grain regeneration is typical of both quartz and plagioclases, but authigenic quartz fills only rare primary cavities or forms discontinuous regeneration rims on clastic grains. Only regeneration rims are typical of plagioclases. Regenerated orthoclase is extremely idiomorphic, which could point to its earliest formation. It is more probable that, in the case under consideration, part of other rock mineral components had been metasomatically replaced by orthoclase at the latest stage of metagenesis. Stilpnomelane, chlorite, muscovite, and chlorite-muscovite packages are present together with authigenic orthoclase. The listed authigenic layered silicates inherit the matrix of clastic micas, are distorted, and envelope clastic grains. Only isolated small laths of authigenic muscovite have distinct facets.

A set of authigenic minerals and their structural position testify to several stages of epigenetic transformations, each of which remained unfinished. The presence of stilpnomelane and orthoclase metasomatism together with the preservation of clastic structures can indicate that the stage of metagenesis is still not complete. Primary clay minerals and clastic micas are completely transformed. Authigenic albite accounts for 20% of total plagioclase content; authigenic orthoclase forms no less than 50% potash feldspars.

THE TECHNIQUES AND METHOD OF SAMPLING

Samples were selected for analysis from the collections of Veis and Pokrovskii (GIN). The whole-rock samples were taken from four stratigraphic levels of natural outcrops (Fig. 2). The Omakhta Formation was studied in exposures located at the southern Uchur depression in the middle reaches of the Idyum River (near the Sivaglikan Creek mouth). The Konder and Omnya subformations of the Totta Formation were sampled at the northern slope of the Omnya uplift (Bol'shoi Aim and Omnya rivers). The Kandyk Formation was sampled at the northern Maya depression (the lower reaches of the Bol'shoi Kandyk and Maya rivers). The samples of the Omakhta, Malga, Tsipanda, and Neryuen carbonate rocks were taken from the conjugate sections (Idyum, Bol'shoi Aim, Aim, and Maya rivers).

In the laboratory, the clay rock samples of about 500 g in weight were crushed to a fraction of 1–2 mm, washed with water in an ultrasonic bath for removal of possible impurities from the surface of fragments, dried, and pulverized in an agate grinder. Carbonate rocks were not preliminarily treated. They were decomposed in 1N HCl for an analysis of Sr isotopic composition.

The contents of Rb and Sr and Sr isotopic composition of all samples were determined by isotope dilution with the use of a MAT-260 mass-spectrometer. The $^{87}\text{Sr}/^{86}\text{Sr}$ values were normalized to $^{87}\text{Sr}/^{86}\text{Sr} = 8.37521$ and were reduced to the value $^{87}\text{Sr}/^{86}\text{Sr} = 0.70801$ in the VNIIM standard (Vinogradov and Chernyshev, 1987). The isotope ratio measured in the course of this work in the above standard, was 0.70812 ± 0.00002 (2σ) for nine independent determinations. The accuracy of the $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios determination was $\pm 1\%$ and ± 0.0002 , respectively. The isochron and errorchron relationships were graded by the χ^2 method (Sokolov and Bujakait, 1986), and errors were determined according to York (1966). A mean square weighed deviation was calculated from the equation $\text{MSWD} = S_{\min}/(n - 2)$, where $S_{\min}$ is the sum of the squares of deviations from an straight line, and n is the number of data points.

The content of radiogenic Ar in samples was determined to have an accuracy of $\pm 1.6\%$ by the method of isotope dilution with the use of the MI-1201 IG special-

Table 1. Rb–Sr characteristics of Riphean siltstones from the Uchur–Maya rocks

Sample no.		ppm		⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr
labora- tory	field	Rb	Sr		
Omakhta Formation					
4230	O-3	195.5	56.0	10.300	0.91200
4231	O-5	250.1	42.28	17.688	1.01326
4233	O-13	196.7	48.91	11.800	0.91822
4234	O-15	221.6	55.48	11.800	0.92185
4235	O-16	191.1	58.09	9.688	0.88948
4236	O-22	181.3	63.85	8.356	0.88205
Kandyk Formation					
4268	40/2E	156.2	97.89	4.654	0.79062
4269	40/24	133.9	97.66	3.997	0.78426
4270	40/50	90.85	77.98	3.395	0.78164
4271	43/3	175.8	81.19	6.330	0.81282
4272	43/7	186.4	75.09	7.268	0.82741
Omnya Formation					
4273	50/A	160.1	77.09	6.063	0.79848
4274	50/G	147.9	72.17	5.970	0.79745
4275	50/E	110.4	73.07	4.404	0.78012
4276	50/4	163.6	69.65	6.862	0.80910
4277	50/2	148.5	70.81	6.123	0.80033
Kandyk Formation					
4193	UM52/A-1	164.5	90.59	5.290	0.77998
4194	UM52/B-2	166.2	92.46	5.238	0.77919
4195	UM52/V-3	127.7	78.75	4.720	0.77404
4196	UM52/G-1	109.6	63.35	5.040	0.77778
4197	UM52/G-2	148.2	82.82	5.213	0.77903
4198	UM52/G-3	153.8	86.88	5.170	0.77790
4200	UM52/3-1	30.39	24.72	3.576	0.76304
4201	UM52/3-2	152.4	84.40	5.260	0.77964
4202	UM8952/2	177.8	93.80	5.526	0.78266

ized mass-spectrometer. This accuracy was controlled by both systematic measurements of standard samples and repeated analyses and the same sample. The concentration of potassium was determined by the flame photometry method with a relative error of not more than 1%, the content of potassium in the sample being above 1.5%. At lower K contents, the error increased to $\pm 2\%$.

For determining C and O isotopic composition, carbonates were decomposed by the standard method in orthophosphoric acid. In addition to calcite, which is decomposed during 1.0–1.5 h, dolomite was analyzed in certain samples. Its time of decomposition was 24 h. The C and O isotopic composition was measured with

a MI-1201V mass-spectrometer for the same volume of CO_2 . The error of determining $\delta^{13}\text{C}$ (PDB) and $\delta^{18}\text{O}$ (SMOW) values was not higher than $\pm 0.2\%$. The NBS-19 and KH-2 standards were used for correlation with the PDB standard (Gerstenberger and Herrmann, 1982). The $\delta^{18}\text{O}$ values were recalculated relative to SMOW from the equation $\delta^{18}\text{O}_{\text{SMOW}} = 1.0308 \times \delta^{18}\text{O}_{\text{PDB}} + 30.86$ (Friedman and O'Neil, 1977).

RESULTS OF THE STUDY

The Rb–Sr system. The results of the Rb–Sr measurements are presented in Table 1 and Fig. 3. Four series of whole-rock samples, each of which has its own stratigraphic position in the section, show linear arrays in the isochron coordinates. Two of them (the Kandyk samples of the Ui Group, and the Omnya samples of the Totta Formation, Kerpil Group) are isochrons; two other series (the Konder samples of the Totta Formation, Kerpil Group, and the Omakhta samples of the Uchur Group) are errorchrons. The position of the points is shown in Fig. 3, and the results of calculations are given in Table 2. The same table presents the accepted age values obtained by different groups of researchers for glauconites and summed up in (Semikhatov and Serebryakov, 1983).

Table 2 shows that the Rb–Sr datings of siltstone whole-rock samples and K–Ar glauconite datings coincide only in the upmost section (in Ui rocks). The difference in dating increases downward the section. In the Omakhta rocks, the K–Ar age of glauconite is 400 Ma older than the Rb–Sr age of claystones. The primary Sr isotope ratios are very high and increase downsection from 0.727 in the Kandyk rocks to 0.764 in the Omakhta rocks.

The results of measurements of Sr isotope ratios in carbonate rocks are given in Table 3. The position of carbonate rock samples in the section is shown in Fig. 2. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios measured for the Kerpil and Lakhandia samples with low $^{87}\text{Rb}/^{86}\text{Sr}$ ratios (< 0.03) vary from 0.7055 to 0.7064. The correction for the accepted stratigraphic age of these rocks is relatively insignificant, and their corrected Sr isotope ratios are almost unchanged (0.7055–0.7061). The Uchur carbonate rocks show high Rb/Sr ratios and greatly dissimilar and high Sr isotope ratios.

The K–Ar system. The results of K–Ar determinations are given in Table 4. In almost all cases, the K–Ar age is higher than Rb–Sr age for the same whole-rock samples. At the same time, the measured K–Ar age of whole-rock samples agrees well with the glauconite age and accepted stratigraphic age of rocks. Thus, two of three datings of the Omakhta rocks correspond to the accepted age, and one of them is slightly younger. Two datings of the Omnya rocks virtually coincide with the accepted stratigraphic age, and only the K–Ar whole-rock ages of the youngest Kandyk Formation

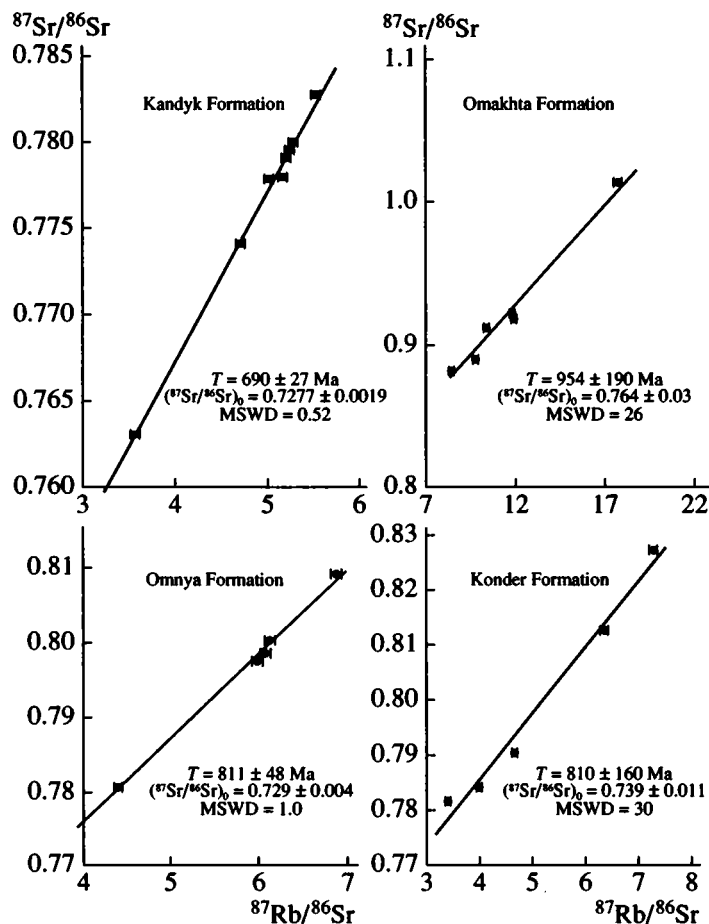


Fig. 3. Rb-Sr isochron diagrams for four subdivisions of Riphean rocks in the Uchur-Maya region.

(Ui Group of the Upper Riphean) are higher than the glauconite ages.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. The carbon and oxygen isotopic composition was determined for 49 carbonate rock samples of mostly calcite composition (Table 5, Figs. 4, 5). The samples taken cover virtually the entire Riphean succession of the Uchur-Maya region, but characterize it inadequately because of sparse sampling. Figure 4 distinctly indicates that the $\delta^{13}\text{C}$ values regularly increase up the section from $-0.7 \pm 2.7\text{‰}$ in the Omakhta Formation to $+5.0\text{‰}$ in the lower

Lakhanda Group. This increase is accompanied by secondary fluctuations.

The oxygen isotopic composition is distinctly variable in rocks of different formations. Thus, the average $\delta^{18}\text{O}$ values in the Omakhta and Tsipanda formation, mostly composed of dolomite (25.6 ± 0.8 and $26.8 \pm 0.8\text{‰}$, respectively) are by 2–3‰ higher than those in the Malga Formation and the lower part of the Lakhanda Group mainly composed of limestones (23.9 ± 0.6 and $24.1 \pm 1.3\text{‰}$, respectively). At the same time, calcite and dolomite fractions analyzed in one and the

Table 2. Results of Rb-Sr isochron calculations

Formation, subformation	Number of points	Rb-Sr, Ma	$(^{87}\text{Sb}/^{86}\text{Sr})_0$	MSWD	K-Ar*, Ma
Kandyk	9	690 ± 27	0.7277 ± 0.0019	0.5	700–760
Omnya	5	811 ± 48	0.7289 ± 0.0039	1.0	979–1020
Konder	5	810 ± 160	0.739 ± 0.011	30	1000–1100
Omakhta	6	954 ± 190	0.764 ± 0.029	26	1360

Note: An asterisk indicates a glauconite age, based on Semikhatov and Serebryakov (1983).

Table 3. Content of Rb and Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in Riphean carbonates of the Uchur–Maya region

Sample no.		Formation	ppm		$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_0$
laboratory	field		Rb	Sr			
4191	om-3	Omakhta	0.70	14.32	0.142	0.70836	0.70559
4190	om-10	"	0.55	21.67	0.074	0.70703	0.70559
4189	ml-4	Malga	1.02	139.1	0.022	0.70640	0.70608
4188	zp-4	Tsipanda	0.59	56.10	0.030	0.70593	0.70550
4187	zp-9	"	0.53	62.10	0.025	0.70631	0.70595
4186	lh-6	Lakhanda	0.29	140.2	0.006	0.70659	0.70650
4185	lh-13	"	0.33	192.0	0.005	0.70560	0.70553
4184	lh-17	"	2.15	52.29	0.119	0.70669	0.70499

Table 4. Results of the K–Ar whole-rock age determinations in siltstones of the Uchur–Maya region

Sample no		Formation, sub-formation	ppm		Age, Ma		
laboratory	field		K, %	Ar, nmm ³ /g	K–Ar	Rb–Sr	Stratigraphic*
4200	52/3-1	Kandyk	0.93	0.0527	1080	700	700
4202	8952-2	"	3.92	0.171	870		
4275	50/E	Omnya	2.44	0.1425	1090		
4276	50/4	"	3.33	0.195	1095	800	1000
4270	40/5	Konder	8.14	0.221	590		
4230	O-3	Omakhta	6.76	0.521	1335		
4231	O-5	"	6.90	0.546	1360	950	1360
4234	O-15	"	6.17	0.365	1105		

Note: An asterisk indicates a glauconite age, based on Semikhatov and Serebryakov (1983).

same sample do not show such stable differences in an oxygen isotopic composition.

On the $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ coordinates (Fig. 5), the data on the above rocks form individual fields without any common trend. The positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is clearly defined in the Omakhta and Malga rocks. In the Tsipanda rocks, the wide spread in $\delta^{18}\text{O}$ values is accompanied by uniform distribution of the $\delta^{13}\text{C}$ values. On the contrary, very wide variations in the carbon isotopic composition are observed in the Lakhanda rocks at a relatively stable (for only one exception) oxygen isotopic composition.

DISCUSSION OF THE RESULTS

The results obtained bring up a number of questions to be discussed. First of them is the significance of the obtained isochron and errorchron dependencies of bulk samples of terrigenous rocks for the assessment of age. If this question is answered positively, another question arises on an event or events that reflect the calculated age values. Then, it is necessary to consider possible causes of discrepancies between the Rb–Sr and K–Ar whole-rock datings and K–Ar glauconite age determinations. Last and important is the relation of all the

known and newly obtained isotopic datings of the Riphean rocks in the Uchur–Maya region to the time of rock formation. It is also necessary to discuss the Sr isotope ratios of carbon and oxygen in carbonates as possible correlation indications of the Riphean rocks.

Rb–Sr. We positively answer the first question proposed. Figure 3 along with the master plot (Fig. 6) clearly indicate that the slopes of the isochron plane lines, corresponding to four stratigraphic subdivisions, namely, Kandyk Formation (R_3), Omnya and Konder subformations (R_2) and Omakhta Formation (R_1), increase in a stratigraphic order. The Konder and overlying Omnya subformations of the Totta Formation show the same isotopic age, but all four series of samples have distinctly different initial Sr isotope ratios. It is absolutely evident that a contingency is ruled out of this regularity, and each line obtained on the Rb–Sr isochron coordinates reflects a real event in rock life. This event has certainly no relation to sedimentation age but reflects the stage of secondary rock transformation. We previously faced this phenomenon during the study of the Riphean rocks in other Siberian regions; e.g., Katanga trough (Vinogradov *et al.*, 1994), Patom highland (Vinogradov *et al.*, 1996), and Baikit uplift (Vinogradov *et al.*, 1998). But in all preceding cases, the

Table 5. Carbon and oxygen isotopic compositions in Riphean carbonates of the Uchur–Maya region

No.		$\delta^{13}\text{C}$, ‰ (PDW)	$\delta^{18}\text{O}$, ‰ (SMOW)	No.		$\delta^{13}\text{C}$, ‰ (PDW)	$\delta^{18}\text{O}$, ‰ (SMOW)
ordinal	field			ordinal	field		
1	1/93	–1.6	24.9	26	zp-13	0.6	25.6
2	6/93	–1.9	24.9	27	zp-15	0.3(0.1)	26.7(26.7)
3	10/93	–2.7	24.5	28	zp-17	0.6	25.8
4	24/93	–2.0	24.5	29	zp-19	0.6(0.5)	26.2(26.6)
5	12/93	–2.1	25.7	30	lh-1	0.5	23.3
6	17/93	–2.3	25.6	31	lh-2	0.8	24.5
7	19/93	–2.1	26.4	32	lh-3	0.5	23.5
8	om-1	–1.3	25.7	33	lh-4	–0.1	19.8
9	om-3	–1.1	26.3	34	lh-5	0.3	23.5
10	om-5	–1.1(–1.1)	26.1(26.6)	35	lh-6	0.5	24.4
11	om-8	–0.7	25.3	36	lh-7	0.8	24.5
12	om-10	–0.9	26.9	37	lh-8	–1.4	24.6
13	ml-1	–1.6	23.0	38	lh-9	–2.7	24.2
14	ml-2	–1.0	24.2	39	lh-10	–2.6	23.8
15	ml-4	0.8	24.1	40	lh-11	–0.4(–0.2)	23.6(25.6)
16	ml-5	0.1	24.9	41	lh-12	0.0	25.7
17	ml-6	–0.4	23.6	42	lh-13	3.8	24.1
18	ml-8	0.1	24.6	43	lh-14	5.0	23.4
19	ml-10	–1.0(–0.9)	23.7(24.3)	44	lh-15	4.2	25.1
20	ml-11	–1.3(–1.3)	23.3(23.7)	45	lh-16	3.6	23.2
21	zp-1	0.6	27.2	46	lh-17	1.2 (1.2)	25.8(28.0)
22	zp-4	0.6	27.0	47	lh-18	1.7	25.1
23	zp-7	0.5	27.2	48	lh-19	0.7	25.8
24	zp-9	0.9	28.0	49	lh-20	0.2(0.5)	25.2(26.6)
25	zp-11	1.0	27.4				

Note: Sample location. (1–12) Omakhta Formation: (1–7) Idyum River near the Sivaglikan River mouth, (8–12) Bol'shoi Aim River near the junction with the Malyi Aim River; (13–20) Malga Formation in the lower reaches of the Aim River; (21–29) Tshipanda Formation in the lower reaches of the Aim and Maya rivers below the Aim Settlement; (30–49) Lakhanda Group in the Maya River between the Neryuen and Emelekyuen river mouths. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are given for calcite, except for dolomite (in brackets).

transformation stage affected the entire Riphean succession regardless of rock age. We should suppose that these were great events of regional and, possibly, even planetary scale.

In the Uchur–Maya region, the Rb–Sr system of the Riphean rocks was sequentially reconstructed from formation to formation. This is corroborated by a regular series of calculated age values and primary Sr isotope ratios. A similar phenomenon can be easily explained by subsidence of the sedimentary basin and sequential

passing of rocks through a certain critical level of depth and temperature. The study of younger rocks indicated that one of such critical levels can be the hydromicritization of clay material (Drits and Kossovskaya, 1990; Kossovskaya and Shutov, 1971; Shutov *et al.*, 1971). Much evidence exists illustrating that this process sharply accelerates when a certain boundary depth and, consequently, temperature is reached. While studying Tertiary clay rocks in the Texas coastal region, it was shown (Ohr *et al.*, 1991) that the smectite–illite transformation distinctly accelerates at a depth of about

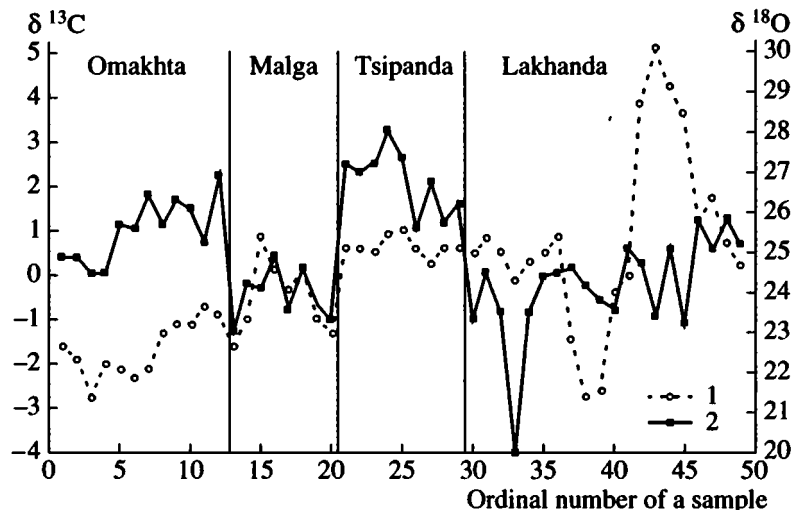


Fig. 4. Distribution of isotopic compositions of (1) C and (2) O in the Riphean carbonate rocks.

2400 m, corresponding to a temperature of about 70°C. The Rb–Sr system is reconstructed at the same depth, and a distinctly decreased isotopic age is recorded in the rocks. Slightly higher temperatures of smectite–illite transformation (80–100°C) are referred to in (Aronson and Elliot, 1994). The Rb–Sr and K–Ar analysis of an illite fraction finer than 2 μm from the Ordovician and Silurian shales (Evans, 1994) indicated that the age of about 400 Ma is the time of the passing through the 260 ± 30°C isotherm.

While studying the Oligocene Frio Formation (Morton, 1985), it was concluded that smectite is transformed into illite as sediments submerge to a depth of 3.5 km, and that illite content remains constant (about 80%) to a depth of 6 km.

The transformation of smectite into illite in the Solton See hydrothermal field is considered in (Yu-Chyi Yau *et al.*, 1987). It was shown that smectites began changing into illites at 70°C, and smectites or smectite–illite-type mixed-layer minerals are absent at a temperature above 230°C. Layered silicates are represented only by illite.

Kholodov (1983) very thoroughly studied the catagenetic transformation of clayey rocks in the Mesozoic sections of the Eastern Ciscaucasia region. According to his data, secondary alterations in clay minerals are most prominent at a depth of 3700 m and 170°C. However, the transformation depth depends on many factors and varies from 1200 to 3700 m, corresponding to a 100–180°C temperature interval.

From this brief review it follows that the transformation of a clayey material sharply accelerates and its isotopic systems are reconstructed at a depth of the order of 2.5–3.0 km and at a temperature of about 80–100°C. Although the estimates available are approximations, the gist of the matter remains unchanged. The results obtained indicate that the subplatformal Riphean rocks of the Uchur–Maya region relatively slowly subsided. The time required for the sediments to pass through at a critical depth and to reach the temperature of smectite–illite or other transformations was sequentially recorded in the Rb–Sr systems of clayey rocks. If rock thicknesses are assumed to be preserved to until the present time, though they in fact decrease with time (Kholodov, 1994), we can calculate the rate of subsidence.

The rock thickness between the sampled Kandyk and Totta formations is 950–1500 m. The difference in estimates depends on variability in thicknesses (Semikhatov and Serebryakov, 1983). The Rb–Sr age for these formations to pass through a critical depth differs by 110 Ma. Thus, in the Riphean, this part of the Siberian Platform

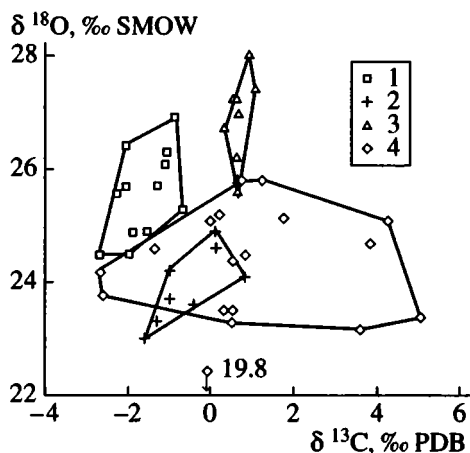


Fig. 5. Relationship between O and C isotopic compositions in carbonate rocks of the Uchur–Maya region. (1) Omakhta Formation, (2) Malga Formation, (3) Tsipanda Formation, (4) Lakhanda Formation.

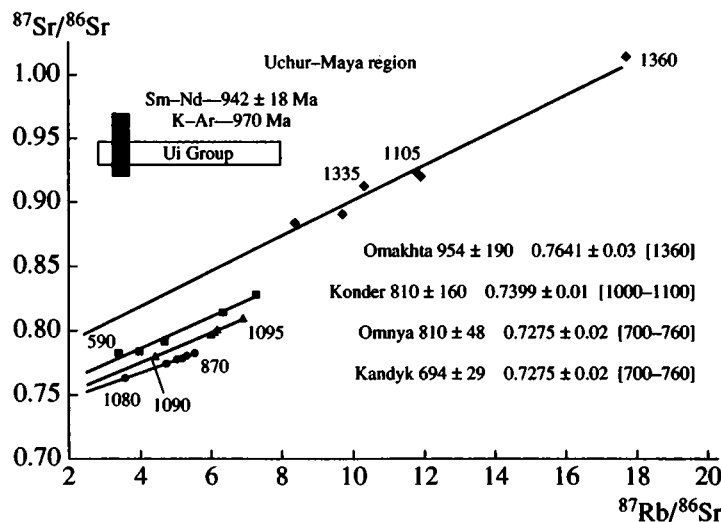


Fig. 6. Master isochron diagram of isotope (Rb-Sr and K-Ar) ages of the Riphean rocks in the Uchur-Maya region. K-Ar ages are shown near corresponding points. K-Ar glauconite datings are displayed in brackets as stratigraphic ages (Semikhatov and Serebryakov, 1983). The diabase dike, which intrudes the Upper Riphean rocks, and its age (after D.I. Zhuravlev, see the text) are schematically shown in the upper left corner of the figure.

subsided at a rate of 9–14 m during 1 Ma. Without a significant error, we can apparently assume that the critical depth of rock transformation with the reconstruction of the Rb-Sr system is 3000 m. At a calculated rate of subsidence, a depth of 3000 m will be reached within 200–300 Ma.

K-Ar. Despite the wide spread in the obtained K-Ar whole-rock datings of clays, we can state that they well agree with the glauconite age determinations. It is well known that K-Ar dating of bulk samples of terrigenous rocks can give very different results. If mineral components of the provenance are well preserved in the source regions, rock age will be overestimated relative to sedimentation time. Rock age will be underestimated in the case of intense post-sedimentation mineral formation. The combination of authigenic and well-preserved terrigenous particles can result in the obtaining of randomly dispersed isotope data not subject to interpretation. Our estimates could be referred to such a variant, if the results of K-Ar glauconite age determinations were unknown. The relationship between both datings is presented in Table 4. It is seen that the upper values of the K-Ar whole-rock datings coincide with the glauconite age determinations for both Uchur (Omakhta) and Kerpyl (Konder and Omnya) rocks.

Hence, we can draw the following conclusions. First, the isotopic (K-Ar) memory of source areas was lost in samples which we randomly selected and analyzed. Authigenic minerals and the products epigenetic transformation of rocks, become a main carrier of K-Ar information. Second, the coincidence of the data of whole-rock samples and globular glauconites indicates that the latter were also transformed at the stage of epigenesis. Consequently, a glauconite age cannot

characterize the time of sedimentation or early diagenesis.

The latter conclusion is far from recent. Numerous indications exist that glauconite, as well as other clay minerals, is subject to secondary epigenetic transformations. During these transformations, glauconite isotopic systems can be disturbed or reequilibrated. As a result, the determined isotopic age proves to be rejuvenated. It can reflect the stage of rocks mineral reconstruction or have no geological sense at all. An ample piece of literature is devoted to this problem (Clauer, 1981; Clauer *et al.*, 1992; Gorokhov *et al.*, 1997; Grant *et al.*, 1984; Laskowski *et al.*, 1980; Morton and Long, 1984; Pasteels, 1985; *et al.*). Its discussion is omitted in this paper. We mention only one of the recent works analyzing the oxygen and hydrogen isotopic composition of glauconites, including those from the Riphean succession of the Uchur-Maya region (Pokrovskii and Ivanovskaya, 1996). It indicated that, in all cases studied, the post-sedimentation isotopic exchange between glauconite-illite minerals and the environment was very intense and took place at temperatures above 70–80°C.

At the same time, the values of both glauconite and whole-rock K-Ar datings clearly depend on the stratigraphic position of a sample. Contingencies should be apparently ruled out here as well as in the above case with Rb-Sr determinations. Certain events in rock evolution are dated by both glauconites and whole-rock samples. These events are probably related to sequential rock passing through a certain critical boundary (depth and temperature), where the K-Ar system of rock was reconstructed, and an isotopic clock was installed at zero.

The comparison between Rb-Sr and K-Ar datings indicates that the K-Ar system of clay minerals is more

stable than the Rb–Sr. Similar cases have been observed in other literature (Pasteels, 1985). However, we should admit that the adjusted ages of both systems are more frequent. The mineral composition of the rocks studied were apparently reconstructed several times, and only the Sr system was affected last time, while the Ar system remained unchanged.

As was mentioned above, age memory of rocks from possible source areas are not observed in the whole-rock samples of the Riphean succession of the Uchur–Maya region. This circumstance can be related to the fact that unaltered clastic potash feldspars are very minor in a rock and would not prominently affect the Rb–Sr system of a whole-rock sample. Such a phenomenon was observed by Gorokhov even in slightly altered Vendian and Lower Cambrian rocks (blue clays) of the Baltic region (Vinogradov, 1997).

A time of rock formation. The isotopic geochronological data available, including those obtained by us, do not allow us to establish the absolute age of Riphean rock formation in the Uchur–Maya region. All known ages characterize the time of rock mineral transformations and, consequently, reflect only the upper age limit of their formation. An age interruption between these events can be very different.

Following the above logic, we should admit that the age of Ui rocks obtained by us and other researchers (about 700 Ma) reflects the stage of their mineral transformation that took place at a depth of about 3 km. In turn, the Ui rocks can be at least by 200–300 Ma older than it was accepted.

This assumption has independent and quite substantiated proof. The data on Sm–Nd determinations of mineral fractions (plagioclase, pyroxene, and rock) for diabase sill, which intrudes Ui rocks, are referred to in (Pavlov *et al.*, 1992). Their isochron age is 942 ± 18 Ma. D.Z. Zhuravlev (IGEM) has obtained a close K–Ar amphibole age of 970 Ma for the same sample. Thus, the upper limit of the Ui rock age is 950 Ma, and the true age of rock formation can be even older. So, the ages of other Riphean rocks of the Uchur–Maya region, including the age of Aimchan rocks should be also changed at least by 250 Ma.

$^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ in carbonates. The isotopic characteristics of carbonate rocks are well utilized for stratigraphic correlation. The remarkable and sometimes unique results of isotopic and geochemical correlation of young and, first of all, Cenozoic rocks have been obtained. But, the older the rocks studied, the less reliable their correlation, especially, concerning Precambrian rocks. The difficulties here are related to two circumstances: we should take into account secondary epigenetic alterations of rocks and solve the problem of interregional correlation of Precambrian sections. The latter circumstance hampers the work of finding reliable correlation criteria. At present, researchers are engaged in accumulating empirical data rather than really using them in stratigraphic constructions (see,

for example, Knoll *et al.*, 1995; Semikhatov, 1995, 1997). Nevertheless, certain Precambrian chemostratigraphic boundaries are reliably characterized, especially when concerning a Vendian–Cambrian boundary where a negative anomaly of carbon isotopic composition is clearly defined (Adams, 1996; Brasier *et al.*, 1996; Derry *et al.*, 1992; Kaufman *et al.*, 1996; Pokrovskii, 1996).

A positive anomaly of carbon isotopic composition was observed in the Upper Riphean carbonate rocks (850–600 Ma) as well as at a level of 2.1 Ga (Baker and Fallick, 1989; Karhu and Holland, 1996). The peak of low $^{87}\text{Sr}/^{86}\text{Sr}$ values (about 0.705) is reliably recorded in an Sr isotopic composition between 800–900 Ma (Asmerom *et al.*, 1991; Derry *et al.*, 1992; Kuznetsov *et al.*, 1997; Veizer *et al.*, 1983). At present, we only have these particular cases of more or less reliable isotopic geochemical correlation of Precambrian boundaries. All other numerous attempts in the application of this method for the Precambrian are far from definiteness, although they can be successful within individual sedimentary basins.

Table 3 indicates that the values of Sr isotopic composition of Tsipanda (Kerpyl Group) and Neryuen (Lakhandia Group) carbonates are very low (0.7055). These values are calculated with correction for a conditional age of 850 Ma. This time condition is insignificant, because the Rb/Sr ratios in the samples studied are low, and, therefore, the Sr isotope ratios measured and corrected for age are close to one another. Tsipanda and Neryuen carbonates compose thick sequences and, judging by the fact that low Sr isotope ratios are reproduced in a series of samples, we can suppose that they are close to primary $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in sea water of corresponding periods slightly changed by secondary processes.

Figure 7 shows the generalized curve of variation in the Sr isotopic composition in Precambrian carbonates. A series of studies is devoted to the problem of Sr isotopic composition evolution in the Precambrian seas (Asmerom *et al.*, 1991; Derry *et al.*, 1992; Gorokhov *et al.*, 1995; Kaufman *et al.*, 1993; Kuznetsov *et al.*, 1997; McCulloch, 1994; Mirota and Veizer, 1994; Veizer, 1989; Veizer and Compston, 1976; Veizer *et al.*, 1983; Veizer *et al.*, 1989; Veizer *et al.*, 1992a; Veizer *et al.*, 1992b). As a basis for plot construction, we adopted a curve from (Derry and Jacobsen, 1988), presented by open circles in Fig. 7. This curve branch, corresponding to the Archean, is drawn to allow for the points from (McCulloch, 1994; Toul *et al.*, 1994), shown by black circles in Fig. 7.

The position of this line is rather conditional for the Precambrian, especially for the interval older than 1 Ga. This time condition was previously addressed in (Vinogradov *et al.*, 1998). A sharp increase in Sr isotopic composition, approximately to 0.7075 at a boundary of 1 Ga, which is related to a mantle event about 900 Ma ago (Veizer *et al.*, 1983), is most disputable. Gorokhov

et al. (1995) tried to substantially decrease this peak. However, the substantiation of the age correlation of points used in this attempt is very problematic (Vinogradov *et al.*, 1998). The last work of Veizer (Mirota and Veizer, 1994), devoted to the study of Sr isotopic composition of Proterozoic carbonates, indicates that the isotopic maximum at a level of 1 Ga is equal to 0.7068 (Veizer and Compston, 1976) and probably shows for the first time that the curve is more complex between 2.5 and 1 Ga. The corresponding points in Fig. 7 have the same numbers as in the original work (Mirota and Veizer, 1994, Fig. 8) with the exception of the points 6 and 7 adopted for the Kotuikan section from (Pokrovskii and Vinogradov, 1991). The latter work substantiated two fundamental concepts.

First, all Kotuikan rocks, which are now referred to Riphean, are older than 1500 Ma. Their lower age boundary can probably be restricted to the latest stage of metamorphic alterations of basement rocks. At the Anabar Shield, it is about 1800–1900 Ma (Rosen *et al.*, 1994). Thus, the Kotuikan Riphean rocks are from 1500 to 1900 Ma old in reality. Second, the primary Sr isotope ratio of the Riphean carbonate rocks is very low (about 0.7046), and it characterizes only the upper boundary of this value for unaltered carbonates.

In Fig. 7, the broken line is drawn for distinction between the points borrowed from (Mirota and Veizer, 1994). The probable location of the Kotuikan points is shown as a horizontal band in Fig. 7. In spite of a great conventionality of the line position, the plot nevertheless provides orientation. Specifically, this figure clearly indicates that carbonates with the age of about 800, 900, and even 1800 Ma can correspond to the $^{87}\text{Sr}/^{86}\text{Sr} = 0.7055$. It is more difficult to interpret the situation based on the data of Mirota and Veizer (1994). Nevertheless, the above conclusion does not contradict the generally accepted Upper Riphean age of the Uir rocks, but poses problems with respect to the age of underlying rocks. Unfortunately, at present, we have no unbiased alternatives among these age intervals.

The Omakhta carbonates compose thin interlayers among terrigenous-clay units, and their Rb–Sr systems are most probably disturbed due to terrigenous host rocks. This apprehension follows from high $^{87}\text{Rb}/^{86}\text{Sr}$ ratios in the Omakhta carbonates. Therefore, it is difficult to interpret their Sr isotope ratios.

It is furthermore more difficult to interpret our data on carbon isotopic composition, because a detailed variation curve in $\delta^{13}\text{C}$ in the Upper Precambrian is still unavailable. The positive anomaly established in the upper Lakhanda Group is a prospective stratigraphic datum mark. A similar anomaly is also traced in the northern Yudoma–Maya trough at the Belaya River, (Podkovyrov, 1997; Podkovyrov and Vinogradov, 1996) 300 km from the site of our Lakhanda carbonate samples.

Relatively low values of $\delta^{13}\text{C}$ in Omakhta carbonates are also traced over large distances within the

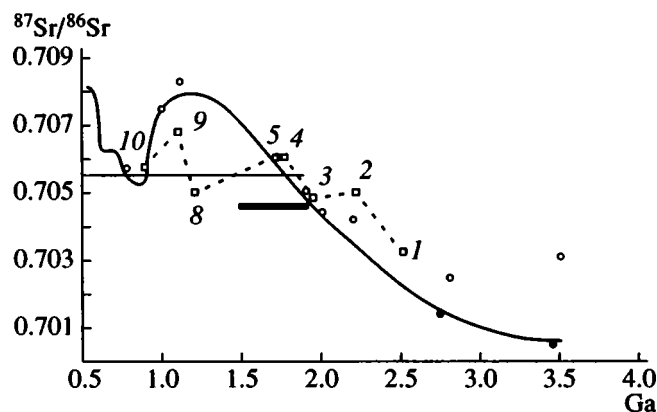


Fig. 7. The schematic curve of variation in the Sr isotopic composition of the Precambrian sea water (explanations are given in the text).

region. The observed correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ambiguously indicates that this correlation is secondary, because a similar relationship is often observed in recent carbonates (Talbot, 1993) which can be caused, specifically, by variations in basin salinity.

It is known that an oxygen isotopic composition of sedimentary carbonates is extremely subject to post-sedimentation alterations. All carbonates dealt with in this paper are altered to a certain degree. We suppose that it is secondary changes that are responsible for sharp negative anomalies of $\delta^{18}\text{O}$, especially typical of the Lakhanda Group. The established difference in an oxygen isotopic composition between the dolomite- and limestone-rich rocks studied can have different explanations. The $\delta^{18}\text{O}$ value of dolomites is by 3–6‰ higher than that of calcites at an isotopic equilibrium of 25–50°C. These values are commensurable with a difference between dolomite and limestone formations, which can be inherited at the stage of sedimentation or early diagenesis. Otherwise, we should suppose that limestones are more intensely altered than dolomites or are of a secondary (with respect to dolomites) origin.

CONCLUSION

The Riphean rocks of the Uchur–Maya region studied were accumulated during a relatively slow subsidence of this Siberian Platform segment. This resulted in the accumulation of thick sediments. The prolonged hiatus (more than 600 Ma) in sedimentation within the Uchur depression between the Uchur and Yudoma periods is caused by the pre-Yudoma erosion. During the subsidence, the rocks passed through certain critical depths (and temperatures) when the processes of secondary mineral transformations were accelerated and the isotopic systems were reconstructed. There were evidently several such boundaries, and different isotopic systems differently responded to mineral transformations. It is difficult to reconstruct the entire succession of sec-

ondary transformations. We can only state that the Upper Riphean rocks underwent a stage of deep epigenesis, and the Lower Riphean rocks experienced a stage of metagenesis.

Secondary transformations almost absolutely destroyed the isotopic memory of the age of rocks from source areas across the entire Riphean succession of the Uchur–Maya region. These transformations affected not only clay but also fine sand fractions of terrigenous rocks. This made it impossible to establish the age of sedimentation by the data on the rocks themselves. All the available isotopic datings of sedimentary rocks characterize the stages of secondary transformations. The temporal interval between two events (rock formation and its secondary transformation) cannot be exactly established. Judging by the estimates obtained, such an interval can reach hundreds of millions of years.

The isotopic systems of carbonate rocks are more conservative and sometimes can keep information regarding the time of sedimentation. We suppose that the established maximum of the $\delta^{13}\text{C}$ values in the lower Lakhanda Group reflects primary sedimentation conditions. This level can be prospective from the viewpoint of the chemostratigraphic correlation of Lakhanda rocks.

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The X-ray Diffraction Characteristics of Naphthides

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Abstract—The X-ray phase composition of naphthides has been studied over the entire lithogenetic range from petroleums to higher anthraxolites and graphite. The basic components of the objects are the hydrocarbon polynaphthene phase (N_{ph}) and amorphous graphite phase (G_{ph}), whose concentration increases with the growth of the level of catagenetic transformations. It has been shown that resins and asphaltenes represent a mixture of two phases, N_{ph} and G_{ph} , which are in certain quantitative ratios. The values of these ratios are virtually independent of either the age or the depth of petroleum occurrence. We have established the specific character of the phase composition of oxycerites, including the rare fibrous variety, which, in addition to N_{ph} and G_{ph} , contains a structurally-disordered hydrocarbon phase and one more hydrocarbon component with $d = 8 \text{ \AA}$. Ozocerites represent a homogeneous mixture of high-molecular-weight paraffins of N_{ph} and G_{ph} .

INTRODUCTION

In accordance with the definition given by Uspenskii *et al.* (1964) and by Kalinko (1987), the term “naphthides” unites hydrocarbon gases, gas hydrates, gas condensates, petroleums, and natural bitumens. However, a number of researchers (Muratov, 1970; Kartsev, 1978) include only petroleums proper and products of their weathering and catagenetic transformations in the concept “naphthides”. The author of this work follows the latter approach, since gases are independent products of hydrocarbon generation with their own forms of existence and transformation within the Earth’s interior. Therefore, this work will be devoted to the results of the investigation of naphthides in the sense of Muratov and Kartsev.

Petroleums, especially their light fractions, have been studied fairly thoroughly. However, natural viscous and solid naphthides (asphalts, asphaltides, kerites, and anthraxolites), which were devoid of any practical significance for a long time, have not been adequately investigated. Meanwhile, it has been established that they are directly involved in the formation of ore occurrences of a number of elements and can serve as migratory indicators, which is important in prospecting for hydrocarbon fluid deposits.

The data of group and element analyses were mainly used in order to determine the diagnostic criteria for naphthides. However, these data have limited potential for the diagnostics of such complicated systems. The application of X-ray methods to these systems opens up new possibilities for studying their phase composition. Thus, quantitative X-ray phase analysis (QXPA), along with the certain diagnostics of any individual carboniferous object, allows us to follow the dynamics and mechanism of transformation of various genetic types of caustobioliths.

The aim of this work is to demonstrate the possibilities of using XRD methods to identify naphthides and to study the character of X-ray phase transformation in this genetic series over the entire lithogenetic range from petroleums to higher anthraxolites and graphite.

METHODS OF INVESTIGATIONS

All the investigations were accomplished on a DRON-1.5 X-ray diffractometer (Cu radiation) with the use of a PR-14M computer and collimation according to Korolev (1995). Application of the specified means and stringent regimes of discrimination made it possible to eliminate “spurious” radiation from the diffraction spectrum, especially from the low-angle region (up to $0.5^\circ \theta$), while simultaneously retaining considerable transmission of the instrument, which is very important in the study of weakly scattering objects.

Powder preparations were obtained by packing aluminum cuvettes with a volume of $17 \times 17 \times 1.5 \text{ mm}^3$. Liquid objects were studied in a special cuvette, whose design is described elsewhere (Bogatyrev *et al.*, 1982).

The diffraction spectrum of the majority of natural carbonaceous substances represents a superposition of principal maximums of various phases merging into one wide halo in the interval from 2° to $15^\circ \theta$. The overlap of reflections significantly hampers the processing of diffraction spectra of such objects.

In order to perform qualitative and quantitative analyses, it is important to know the angular position and intensity of the principal reflections of each component. When the diffractometers are not equipped with a computer outlet, a complicated diffraction maximum can be decomposed into its components by the method of iterations through the approximation of experimental profiles of reflections.

A considerable number of works, in which the approximation of real reflections from various crystalline substances was accomplished using a number of bell-shaped functions, have been published recently. In this case, the approximations were most often performed more successfully when a combination of these functions was used. Careful mathematical analysis of a number of bell-shaped functions (Lorentz, modified Lorentz, Gauss, pseudo-Foight, and Pearson) showed that the experimental profiles of reflections of crystalline objects, such as zirconium dioxide, kaolinite, and dickite, can be approximated to high accuracy using the superposition of two Gaussians (Salyn', 1988). Therefore, a reflection profile may be represented as the result of adding two bell-shaped functions with different angles, where half-width of the lower part is twice as much as that of the upper part.

By applying the QXPA method to the study of amorphous carbonaceous substances, the author successfully decomposed a complicated maximum using the iteration method (Korolev, 1995), the essence of which is as follows.

Assume that the diffraction reflection $Y(x)$ consists of two superimposed maximums, whose profiles can be described, respectively, by the functions $y_1(x) = f(x, \Delta_1)$ and $y_2(x) = f(x, \Delta_2)$ depending on the angular width Δ_j :

$$y_1(x) + y_2(x) = Y(x). \quad (1)$$

Condition (1) must be fulfilled if the Δ_j values are chosen correctly. At the first stage of decomposition, we use trial values Δ_1' and Δ_2' , which, after substitution into (1) and analysis of the deviations of the sum $y_1' + y_2'$ from $Y(x)$, are corrected to yield Δ_1^2 and Δ_2^2 . These evaluations are refined to Δ_i^1 and Δ_i^2 , where i is the iteration number. The fitting process terminates at $i = n$, when equality (1) is fulfilled within the specified accuracy at any x point of the reflection spectrum.

Analysis of numerous processed experimental data showed that the profiles of all hydrocarbon phases can be described by symmetrical bell-shaped Gaussian functions.

The only exception is a graphite-like phase, for which the reflection profiles, as for any layered system (*Rentgenovskie...*, 1965), are asymmetrical, and the trend of low-angle intensity drop depends on the reflection index. Thus, a more gently sloping "tail" is observed in the basal 00l reflections on the low-angle side, while in the hk reflections, a gentler slope is observed on the wide-angle side.

After analyzing the 002 reflection profiles in a large number of anthracite and technical carbon specimens, it has been established that the coefficient of asymmetry $K_a = \Delta_r/\Delta_l$, where Δ_r and Δ_l are the half-widths of the right-hand and the left-hand parts of the reflection, respectively, varies within 1.2–1.6 (average, 1.4). A close value of

asymmetry ($K_a = 1.3$) was obtained by Dubovik *et al.* (1976).

The evaluation of errors related to the specified method showed that the error in determining reflection intensities depends on the content of a particular phase in the mixture. Thus, for a phase content of more than 20%, the relative error does not exceed $\pm 5\%$. The values of interplanar distances d and reflection intensities were used to identify the phases and determine their content, as well as to obtain other XRD characteristics, such as the dimensions of coherent scattering regions L and the degree of anisotropy T (Korolev, 1989).

RESULTS AND DISCUSSION

Based on the analysis of diffraction spectra of the naphthides studied by the author and published data, the following XRD phases were identified.

The polynaphthene phase (N_{ph}). The phase is diagnosed from the principal reflection with $d \sim 4.8$ Å, which is analogous to the principal reflection (the γ -band) of the pure sapropelic variety (Olenek boghead), whose structure was studied in detail using the methods of XRD analysis (Korolev, 1989) and can be described as follows.

The basis of the Olenek boghead structure is formed by flat hydrocarbon networks ~ 25 Å in diameter, consisting of two polymeric patterns with different types of joints between naphthene cycles, thereby producing the **clathrate** structure. In the loose *A* pattern, naphthene hexagons are separated by methylene chains; the *B* pattern represents a condensed system consisting of similar naphthene cycles. The C–C distance in this complicated flat molecule is 1.50 Å. The hydrogen atoms adjacent to carbon atoms are arranged uniformly on both sides of the carbon skeleton, since taking into account a similar arrangement of hydrogen atoms in the model improves the coincidence of estimated and experimental intensities. The molecule has four such neighbors arranged parallel to each other at a distance of 5.05 Å, forming a paracrystallite. The basic bonds of these paracrystallites are paraffin chains threaded through perforated flat molecules, which are retained by the Van der Waals forces. Introducing paraffin chains into the model, on the one hand, improves the coincidence between the estimated and measured reflection intensities (the confidence factor value with the thermal correction $R = 12\%$) and compensates for the deficiency of hydrogen in the flat molecules, on the other hand.

Therefore, X-ray scattering of the polynaphthene phase represents the diffraction interaction of two clathrately-jointed flat petroleum-bearing patterns with paraffin chains of normal structure and union with the latter into a single complex.

In petroleum, their components, and in some viscous and solid naphthides, the analogous phase is characterized by the principal reflection $d = 4.8$ – 5.2 Å. A similar scatter of the d values was also noted by other

researchers (Yen *et al.*, 1961). Higher d values in petroleum in comparison with sapropelic substances (boghead) are due to a higher value of the average distance between the flat polynaphthene molecules, which are bonded by means of heteroatoms and organic chains.

The graphite-like phase (G_{ph}). This component is characterized by the interplanar distance $d_{002} = 3.70\text{--}3.35$ Å, which diminishes with increasing graphitization level, i.e., metamorphism grade (Korolev, 1989). The structure of this phase is very similar to that of graphite; i.e., it is composed of analogous hexagonal networks with C–C distances equal to 1.42 Å, as in graphite, but with negligible dimensions of the coherent scattering regions (L_{crs}), ($L_{002} = 18\text{--}30$ Å), especially at the early stages of graphitization (Korolev, 1989). Moreover, in contrast to graphite, these networks are randomly displaced with respect to each other in the ab plane, which is one more criterion of amorphism. A graphite-like phase is the most typical component of many natural and synthetic carbonaceous substances (Korolev *et al.*, 1990).

The intermediate phase (I_{ph}). This constituent, represented in the spectra by one wide halo with $d \sim 3$ Å, was first detected and described by Korolev (1989) as a completely structurally disordered amorphous phase. It is a group of widely diverse organic molecules and their fragments. The compositional differences of molecules brings this phase close to an almost completely amorphous system with weak diffraction due to the absence of coherent interaction between organic molecules with different structures. The I_{ph} is analogous to the amorphous component that is characteristic of polymers.

The oxygen-bearing hydrocarbon phase O_1 . The reflections with $d \sim 8$ Å are registered in the diffraction spectra of oxycerites, coals, and some naphthides. Since this phase does not exist in pure form, it has proved impossible to decode its structure.

The XRD characteristics and the results of quantitative analysis of the studied objects are presented below.

Petroleum and Their Components

There are practically no published data on XRD studies of various petroleum fractions, with the exception of asphaltenes. In this connection, the author has completed the first systematic XRD study of both asphaltenes and lighter fractions—resins, oils, petroleum, high-viscosity petroleum (HVP), and malthas (Korolev *et al.*, 1979; Korolev and Amerik, 1993). The petroleum and their components originated from 40 wells in various petroleum basins (Western Siberia, Urals-Volga region, Ukraine, Belarus), rocks of different ages (from Cretaceous to Devonian) and various depths (from 100 m to 4.5 km). We investigated the following components of petroleum and resin: oil fraction (7 specimens), chloroform fraction (20), alcohol-benzene fraction (6), benzene fraction (32), and asphaltenes (29). Additionally, nine specimens of asphaltenes

extracted from various Devonian rocks in the Volga-Urals region were analyzed. The samples of different petroleum studied for the first time by the XRD method included the following varieties: ordinary naphthene (6 samples), high-paraffin (3), high-viscosity (3), and malthas (2).

Oils. The diffraction spectrum of oils is fairly similar to that of petroleum and contains the principal reflection with $d = 4.8$ Å corresponding to polynaphthene structures (Fig. 1a). In a number of cases, ordinary paraffin is present as an impurity (up to 6%). All the studied specimens of oils are characterized by the total absence of the amorphous G_{ph} . The average values of basic XRD characteristics are presented in Table 1.

Resins. Depending on the type of solvent used, resins are classified as chloroform, alcohol-benzene, and benzene fractions. Diffraction patterns of all resin fractions are also fairly similar to the spectrum of petroleum and oils (Figs. 1b, 1c). However, along with the dominant polynaphthene phase, the presence of a graphite-like component with $d_{002} = 3.6$ Å was also observed. The content of this phase depends on the solvent type and increases from the chloroform fraction to the benzene fraction (see Table 1).

Asphaltene. The high molecular weight of asphaltene (1250–10000), depending on the technique and type of solvent used, indicates that the carbon skeleton of asphaltene consists of polycyclic condensed systems (Sergienko, 1959).

In early works of the 1940s–1950s, a number of authors, e.g., D. Labout, F. Nellenstein, K. Aleksaryan, and L. Lewis (Yen *et al.*, 1961), performed XRD analysis of asphaltene extracted from petroleum and natural bitumens (naphthides). It was noted that asphaltene extracted from petroleum and natural bitumens (naphthides) produced a diffraction pattern typical of amorphous substances. The presence of two basic maximums with $d = 3.5$ and 4.7 Å was observed. In this case, the similarity between the 3.5 Å reflection and the corresponding principal maximum d_{002} of amorphous carbon was noted. The second reflection was related to the γ -phase.

Eilers (1949) also recorded these reflections in asphaltene. He established the approximate quantitative relationship between the relative intensities of these reflections and the C/H atomic ratio for ten asphaltene extracted from asphalt belonging to different deposits. It was found that the C/H ratio was negatively correlated with the $I_{4.7}/I_{3.5}$ values.

The works of Yen *et al.* (1961) and Erdman (1965) deserve special attention. They confirmed the presence of the above two maximums in asphaltene extracted from petroleum and some solid bitumens. In this case, the γ -phase was referred to by the authors as “hydrogen-saturated carbon.”

An undoubted credit to the authors is the circumstance that they were the first to assess the relative

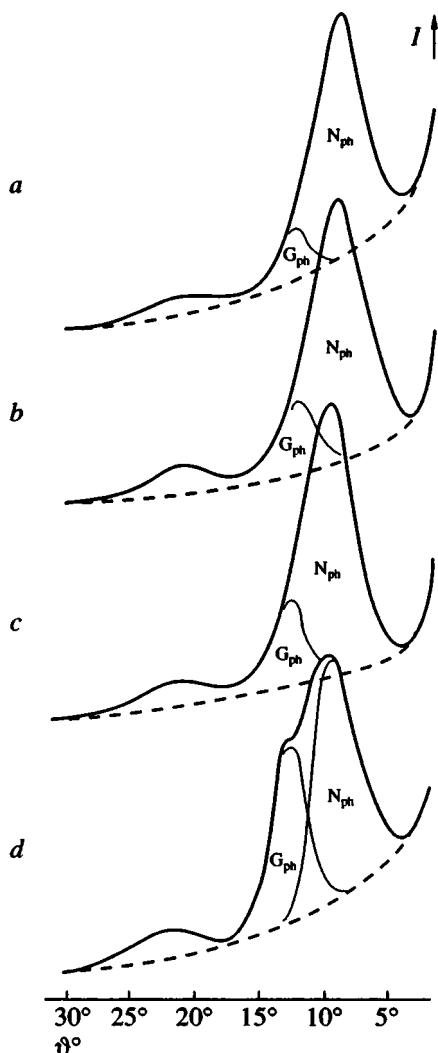


Fig. 1. Diffractograms of petroleum components; Perm oblast, Pavlovskaya-69 well, depth 1419–1428 m. (a) Crude petroleum, $G_{ph} = 5\%$; (b) resins, chloroform fraction, $G_{ph} = 7\%$; (c) resins, benzene fraction, $G_{ph} = 10\%$; (d) asphaltene, $G_{ph} = 35\%$.

quantities of the specified components using the so-called “coefficient of aromaticity”:

$$f_a = \frac{I_{002}}{I_{002} + I_\gamma},$$

where I_{002} and I_γ are the integral intensities of the principal reflections. Analysis of the cited data showed that the average of f_a was 0.36 for eight petroleum asphaltene. The asphaltene extracted from solid bitumens were the exception. Thus, gilsonite has f_a equal to only 0.14, whereas the asphaltene extracted from the residues of cracked petroleum have $f_a = 0.59$, which, as the authors explain, is connected with the splitting off of aliphatic groups during cracking. Finally, for petroleum resins, the f_a value turned out to be 0.22.

XRD investigations of ten petroleum asphaltene carried out by Erdman (1965) show variations in the f_a values between 0.18 and 0.51 ($f_{av} = 0.34$). However, both works lack any explanations for this scatter in the f_a values for asphaltene extracted from petroleum, bitumens, and resin fractions. At the same time, the data reported in Yen *et al.* (1961) also confirm the results obtained by Eilers (1949), i.e., the correlation between the “aromaticity” and the H/C ratio.

As for petroleum asphaltene, such substantial variations in their f_a values may, in our opinion, be due to the use of various extraction techniques, as well as to the errors appearing during processing of fairly complicated diffraction spectra using the method proposed by these authors. Another unjustified assumption made by these authors was that the band with $d = 3.5$ Å was considered as strictly symmetrical, which was later disproved in Dubovik *et al.* (1976) and Korolev (1995).

Subsequently, it was shown by Korolev *et al.* (1979) that asphaltene represented a mixture of the same two X-ray amorphous phases (Fig. 1d), i.e., G_{ph} ($d = 3.5$ Å) and N_{ph} ($d = 4.7$ Å), which are in quantitative relationships ($G_{ph} = 36\%$, Table 1) analogous to those of the average values for petroleum asphaltene reported in Yen *et al.* (1961). According to Rodionova *et al.* (1963), asphaltene extracted from organic matter of sedimentary rocks have a close quantitative ratio of the specified phases ($G_{ph} = 34\%$, Table 1). The fact that two discrete X-ray amorphous phases are present in asphaltene testifies to the absence of so-called “hybrid structures”.

The exception is asphaltene of high-paraffin petroleum, which retain an identical quantitative ratio $G_{ph}/N_{ph} = 1 : 2$ and are characterized by a considerable content of crystalline paraffins with a normal structure (Table 1). The presence of such quantities of paraffins results from imperfections in the technique used to separate paraffin and asphaltene components.

Therefore, on the basis of QXPA data, we may conclude that petroleum fractions, such as resins and paraffins, with the exception of oils, consist of two phases (N_{ph} and G_{ph}). These phases are in certain quantitative ratios, whose values do not depend on the age, type, or depth of occurrence of the petroleum. This statement is supported by Borisova (1981), who also did not detect any substantial differences in the XRD characteristics of asphaltene extracted from West Siberian petroleum of various types and chemical compositions.

According to the data presented in Table 1, a correlation between the G_{ph} concentration and the H/C_{at} ratio value is observed for different petroleum fractions.

Petroleum. The foregoing gives grounds to consider the diffraction of petroleum to be a superposition of diffraction spectra of the gasoline, oil, resin, and asphaltene fractions with $d = 4.9$ – 5.2 Å. In this case, the gasoline and other light fractions are characterized by a basic reflection with $d = 5.0$ – 5.2 Å. The main components of the heavier fractions of petroleum of all

Table 1. The XRD characteristics of petroleum, their components, high-viscosity petroleum (HVP), and malthas

Objects of investigation	Phase composition, %			For G_{ph} L_{002}	H/C _{at}
	N_{ph} 4.8–5.2 Å	G_{ph} 3.6 Å	solid paraffins		
Petroleum components					
Oils	100–94	–	0–6	–	1.65
Resins					
chloroform fraction	93	7	–	24	1.46
alcohol–benzene fraction	92	8	–	25	1.44
benzene fraction	88	12	–	27	1.38
Asphaltenes					
from petroleum	64	36	–	31	1.15
from rocks	66	34	–	30	1.13
from paraffin-base petroleum	32	18	50	25	1.53
Petroleum					
paraffin-base	85	–	up to 15	–	1.93
naphthene	94	up to 3	up to 3	25	1.85
HVP	95	up to 5	–	26	1.70
Malthas	93	up to 7	–	25	1.57

Note: The dash denotes the absence of a component.

types are polynaphthene structures. The G_{ph} is present in a lesser amount (3–7%, Fig. 1a, Table 1). The total amount of G_{ph} in petroleum depends chiefly on the concentration of resinous fractions, the content of which usually increase with the increase in viscosity and specific weight of the petroleum.

As was already mentioned, variations in the d values of the principal reflection of petroleum are caused by the difference in the average distances of intermolecular interaction between naphthene-bearing flat molecules, which, for example, in the oil fraction are still not bound to each other as tightly as in resins and especially in asphaltenes. The average L value of the naphthene phase in petroleum varies from 17 to 23 Å, the maximum values being typical of high-paraffin petroleum. The reflections from solid paraffins of normal structure were also observed in the diffraction spectra of high-paraffin petroleum.

Paraffins of petroleum. These compounds are an integral part of petroleum; their content in some petroleum can reach 80% (Kartsev, 1978; Sergienko, 1959). In order to obtain comparative characteristics, six samples of paraffins extracted from the fractions of Tuimazy and Ozek-Suat petroleum were studied by the XRD method (Korolev and Nosov, 1960). All these paraffins belong to the rhombic system. Along with the common hkl reflections, the basal 001 reflections are registered in the diffraction spectra. These basal reflections mirror the chain length of both the basic paraffin component (Fig. 2a) and other paraffins, i.e., impurities with a lesser or greater number of carbon atoms in the

chain, as well as the amorphous halo with $d = 4.8$ Å corresponding to the polynaphthene phase (Fig. 2b). The presence of impurities is responsible for the noninteger coefficients of the number of carbon atoms in the chemical formula of paraffins, as well as for their decreasing melting temperature (Table 2).

Hence, unlike chemical analysis, XRD analysis makes it possible to distinguish the varieties with even and odd numbers of carbon atoms among normal paraffins by means of basal reflections (Kitaigorodskii, 1955) and to establish the number of carbon atoms as both a basic component and an appreciable impurity in the case of paraffin mixtures. Nevertheless, the data of XRD and chemical analyses are in good agreement (Table 2).

Thus, it follows from the results of X-ray phase analysis that all components of petroleum represent mixtures in which the basic component is the polynaphthene phase with a variable degree of consolidation and paraffins of normal structure. However, the content of the latter in paraffin-type petroleum may be significant. In addition, the graphite phase is present in the resinous and asphaltene fractions.

Viscous and Solid Naphthides

This group of naphthides unites a fairly significant amount of the products of catagenetic transformation of petroleum (Muratov, 1970).

As was already noted, group analysis provides little information about solid naphthides even at the early

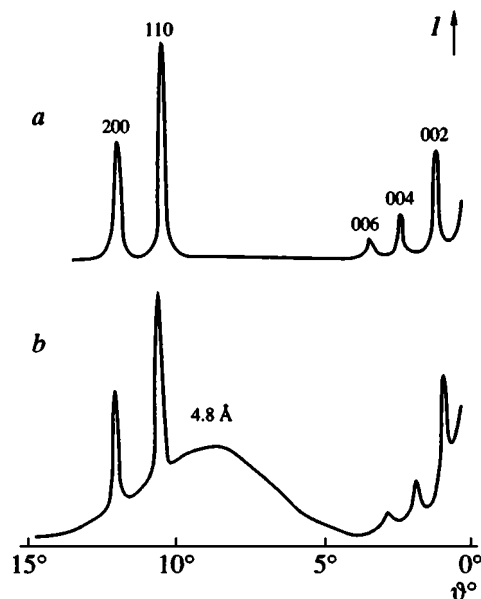


Fig. 2. Diffractograms of solid paraffins from petroleum. (a) Normal paraffin $C_{26}H_{54}$, Tuimazy, D; (b) paraffin $C_{32}H_{66}$ in mixture with the polynaphthene phase, Tuimazy, D.

stages of catagenesis. The differentiation of substances is reduced to dividing them into a number of arbitrary fractions. For carbonaceous substances, which have partially or completely lost their ability to dissolve as a result of higher stages of catagenetic transformation, identification is limited to the data of element analysis. As for higher anthraxolites, even element analysis data do not make any sense, since naphthides at high stages of metamorphism consist entirely of carbon. All of this, unfortunately, makes it impossible to apply unified chemical criteria to the diagnostics of the whole spectrum of natural formations belonging to a given genetic type.

Even the first XRD investigations, carried out by Young (1954), demonstrated that the Debyeograms of some naphthides, such as asphaltites, gilsonite, graha-

mite, and albertite (according to the American terminology,) contain two halos with $d = 4.5$ and 3.5 Å. Based on a visual evaluation of their relative intensities and degree of 'diffuseness,' Young assumed that the intensity increase in the phase with $d = 3.5$ Å was connected with gradual metamorphism of the component with rigid carbon bonds.

Therefore, in his opinion, gilsonites consist almost entirely of large irregular bitumen molecules. The content of rigid carbon is 10–20% in gilsonites, 25–50% in albertite, and as much as 30–50% in grahamite. The suggested sequence of metamorphic transformations of naphthides is as follows: petroleum asphalt–gilsonite–albertite–grahamite–impsonite. The strong 4.54 Å reflection of albertite, according to Ganjavar (1983), corresponds to alicyclic structures.

Atanasyan *et al.* (1982) reported the XRD and chemical characteristics for more than 15 samples of naphthides with lithogenetic transformations varying from asphalts to graphites. To date, more than 28 specimens of naphthides have been studied by the XRD method. Some data of previously studied samples were refined (Atanasyan *et al.*, 1982) and supplemented with new XRD characteristics, such as the diffraction coefficient M , which expresses the degree of organization of carbon atoms in the graphite structure (Korolev, 1989, 1995) and the L_{002} values for the graphite-like phase.

The diffraction spectrum of naphthides at different stages of lithogenesis also consists of two basic reflections (4.8 and 3.6 Å) corresponding to the N_{ph} and G_{ph} (Figs. 3, 4). As follows from Table 3, asphalts are characterized by a G_{ph} content equal to 0–28% and an H/C ratio equal to 1.3–1.5. In asphaltites, the G_{ph} content is 30–40%, and the H/C ratio is 1.2. In kerites, the respective values are equal to 50% and <1 . In anthraxolites at different stages, the G_{ph} content is as much as 90–100%, whereas the H/C value does not exceed 0.4.

Thus, a distinct regularity can be traced, which shows that the intensification of catagenetic transformation results in an increased G_{ph} content with a simultaneous increase in the L_{002} and M parameters of this

Table 2. The XRD and chemical characteristics of petroleum paraffins

Deposit, stratum age	XRD				Chemical		
	d_{002}^e	d_{002}^c	main component	impurity	formula	mol. wt.	melting temperature, °C
Tuimazy, D	35.5	35.2	$C_{26}H_{54}$	–	$C_{25.2}H_{53.8}$	363	49
	43.5	42.6	$C_{32}H_{66}$	–	$C_{31.7}H_{65.4}$	446	64.7
Ozek-Suat, Cr	33.2	33.7	$C_{25}H_{52}$	$C_{20}H_{42}$	$C_{24.6}H_{51.2}$	344	49.9
	33.4	33.7	$C_{25}H_{52}$	$C_{20}H_{42}$	$C_{24.3}H_{50.3}$	340	48.5
	31.1	31.2	$C_{23}H_{48}$	H_{ph}	$C_{22.5}H_{47}$	315	44.3
	29.4	29.3	$C_{22}H_{46}$	–	$C_{21.6}H_{45.2}$	303	29.8

Note: d_{002}^e experimental values; d_{002}^c calculated values.

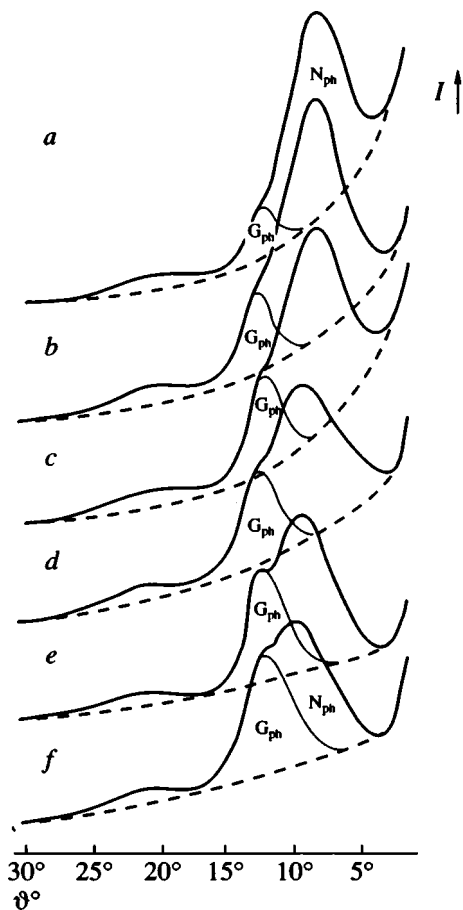


Fig. 3. Diffractograms of naphthides at the medium stage of catagenesis. (a) Asphalt, Kobelyaki, well 206-B, depth 138.7 m, PZ, $G_{ph} = 10\%$; (b) asphalt, Pechora River, Voiskoe deposit, D, $G_{ph} = 20\%$; (c) asphalt, Pechora River, Izhel'sk deposit, D, $G_{ph} = 25\%$; (d) asphaltite, Northern Caucasus, K_1 , $G_{ph} = 30\%$; (e) kerite, Transbaikial region, J_1 , $G_{ph} = 35\%$; (f) kerite, Central Asia, MZ, $G_{ph} = 45\%$.

component and a gradual decrease in the H/C ratio. Quantitative variations in representatives of the humus series also have a similar character (Korolev, 1989).

In order to study the influence of temperature on the transformations of naphthides, asphaltite from the Sadkin deposit was subjected to gradual thermolysis. The X-ray phase composition of the sample studied before and after (in parentheses) thermolysis is as follows (%): G_{ph} , 35 (68); N_{ph} , 56 (14); O_1 , 9 (Korolev and Aref'ev, 1989). As a result of the influence of temperature and N_{ph} destruction, the content of the remaining phases doubled. Pyrolysis resulted in the release of 16.4% of gaseous and 24% of liquid products. The latter, according to chromatography data, correspond to ordinary petroleum hydrocarbons (Korolev and Aref'ev, 1989).

On the basis of these results, the process of X-ray phase transformation of naphthides during catagenesis can be represented as follows. At the initial stages of the transformation, light hydrocarbon fractions volatilize

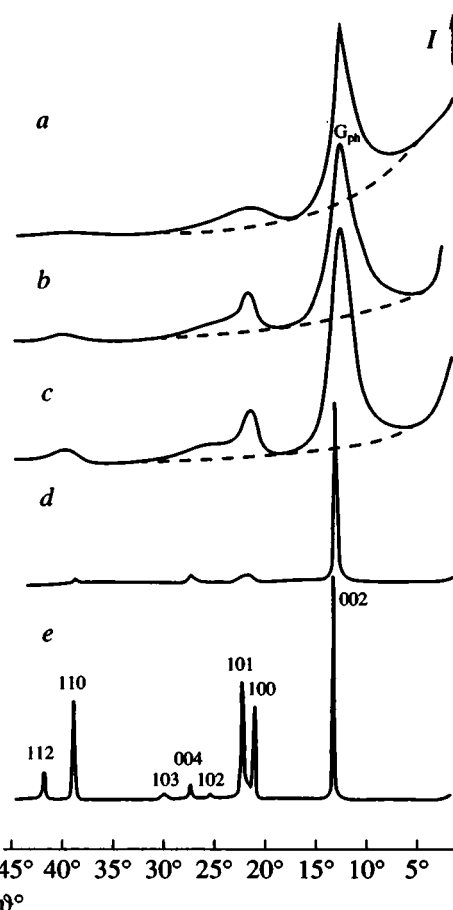


Fig. 4. Diffractograms of naphthides at the high stage of catagenesis. (a) Anthraxolite, Crimea, MZ, $M = 65\%$; (b) anthraxolite, Karelia, PZ, $M = 70\%$; (c) shungite, Karelia, PR, $M = 78\%$; (d) graphite, Central Asia, $M = 82\%$; (e) graphite, Sri Lanka, $M = 98\%$. M is the diffraction coefficient.

from petroleum, with subsequent polymerization of heavier fractions into polynaphthene structures of the N_{ph} type. In what follows, if the temperature increases, N_{ph} destruction takes place, with the release of gaseous and liquid hydrocarbons. Part of this phase transforms into the G_{ph} , which is reflected in a decrease in H/C with a simultaneous increase in the $G_{ph} : N_{ph}$ ratio (Table 3). In the end, only one phase (G_{ph}) remains as a result of the catagenetic transformation. This is the reason why naphthides at the anthraxolite stage are very similar to humus thermoanthracites. During strong metamorphism at higher temperatures, anthraxolites gradually transform into graphite; i.e., the final stable product of lithogenetic transformation of naphthides is graphite.

Thus, a common trend in the catagenetic transformation that affects natural hydrocarbon substances of various genetic aspects, as well as artificial carbonaceous compounds (Korolev *et al.*, 1990) testifies to a unified transformation mechanism. The latter should be

Table 3. The XRD and chemical characteristics of viscous and solid naphthides

Naphthide type	G _{ph} , %	N _{ph} , %	G _{ph} /N _{ph}	M, %	L ₀₀₂	H/C _{at}
Asphalt	10	90	0.11	35	22	1.52
	12	88	0.14	34	22	None
	15	85	0.18	37	23	1.40
	22	78	0.28	41	23	1.29
	28	72	0.39	38	23	None
Asphaltite	30	70	0.43	40	25	"
	35	65	0.54	43	26	"
	38	62	0.61	42	25	1.24
	39	61	0.64	42	27	None
	40	60	0.67	42	27	1.18
Kerite	43	57	0.75	43	26	None
	44	56	0.78	45	26	1.23
	45	55	0.82	45	27	None
	47	53	0.89	43	27	"
	48	52	0.92	Mineralized		0.76
Anthraxolite	48	55	0.92	"		0.67
	92	8	11.5	65	30	0.4
	97	3	32	72	34	0.3
Graphite	100	0	∞	78	36	0.15
	100	0	∞	86	115	0
	100	0	∞	86	130	0
Graphite	100	0	∞	90	170	0

regarded as a process of **graphitization**, which reflects, on the one hand, an increase in graphite-like phase concentration and, on the other hand, the simultaneous growth of the dimensions of its coherent scattering regions (crystallites) and gradual improvement in the spatial ordering of its structure up to transformation into graphite (Korolev, 1989; Korolev *et al.*, 1990).

Oxycerites. According to Uspenskii *et al.* (1964), these compounds represent the products of weathering of asphalt bitumens. They are characterized by incomplete solubility in organic solutions and increased content of oxygen compounds. The total content of oxygen compounds and heteroatoms in some varieties can ~30%.

This group of carbonaceous substances differs sharply from the previous category of substances, first of all in phase composition. Along with G_{ph} and N_{ph}, as in brown coals, completely disordered amorphous intermediate (I_{ph}) and carbon (O₁) phases are present in significant quantities (Fig. 5, Table 4). The existence of I_{ph} and O₁ is indicative of either the influence of oxidative processes on the initial asphalt substance or the genetic specifics of these compounds. The G_{ph} content in oxycerites varies from 17 to 31%. The L_{csr} of this phase is 22–23 Å in all the specimens; i.e., it is virtually

constant and does not depend on the percentage of other components. The G_{ph}/N_{ph} value depends on the H/C_{at} ratio (Table 4). All the studied samples are distinguished by the higher content of heteroatoms (up to 27%).

Fibrous oxycerite (FO). This rare variety was found in the voids of chamber pegmatites of the Volyn region at a depth of ~80 m and identified as fibrous oxycerite (Ginzburg *et al.*, 1987; Luk'yanova *et al.*, 1989). The specimens are lumps of lightweight "rock felt" composed of variable-thickness fibers. The fiber thickness is 0.003–0.015 mm in fine-fibrous varieties, and 0.008–0.05 mm in coarse-fibrous ones. The golden and reddish-brown ribbonlike fibers have the following dimensions: length up to 0.5 mm, width up to 0.015–0.03 mm, and thickness up to fractions of a micrometer. Judging from the morphology of fibrous aggregates, the formation of fine-fibrous ribbonlike masses took place at the closing stage of their development. The chemical composition of FO is distinguished by the increased content of nitrogen, oxygen, and sulfur (Table 4). The fine-fibrous varieties are more carbonaceous than the coarse-fibrous ones, which affects the H/C_{at} ratio.

In order to elucidate the phase composition, the fibrous oxycerites were analyzed by the QXPA method. In the aggregate and quantitative relationship of XRD phases, fibrous oxycerites are, on the one hand, analogous to ordinary oxycerites (Table 4, Fig. 5) and, on the other hand, to humus brown coals (Korolev, 1989), which is confirmed by IR spectra similar to those of brown coal (Ginzburg *et al.*, 1987). Since the fine-fibrous varieties contain more G_{ph}, N_{ph}, and O₁ components, which have the nearest order, and less I_{ph} component (the completely amorphous phase), they are more structurally organized than the coarse-fibrous varieties.

Based on (*Mineralogiya...*, 1973), the development of chamber pegmatites in the Volyn region is associated with the process of granite transformation by gas–water solutions during the formation of a magmatic source and the subsequent pneumatohydrothermal alteration of pegmatite bodies in retrograde temperatures (600 → 200 → 100°C) and pressures (1100 → 200 atm) reduction. In accordance with the conditions for finding FO (Ginzburg *et al.*, 1987) and the sequence of mineral formation in pegmatites (*Mineralogiya...*, 1973), FO formation is connected with the accumulation and polymerization of hydrocarbon gases in hydrothermal solutions, which penetrate into the voids through fissure zones and fractures. Polymerization proceeded at 300–200°C and 500–200 atm. Judging from the FO morphology, polymerization took place in conditions of free contacts of growing individuals with the gas phase. The isotopic composition of carbon δ¹³C in FO is –40.5‰ (Luk'yanova *et al.*, 1989), which is typical of carbonaceous substances from intrusive rocks and testifies to the prevalence of methyl hydrocarbon in its structures, i.e., to the prevalence of methane in the carbon composition of the supplied gases. The polymerization of hydrocarbons and formation of FO could

have proceeded according to the carbene mechanism with the participation of catalysts (Korolev *et al.*, 1990). The role of catalysts can be played by particles of metallic dust and oxides of heavy metals (Fe, Ni, Co, etc.), which have been detected in FO by the spectral analysis (Luk'yanova *et al.*, 1989).

Thus, the XRD composition of oxycerites, including their fibrous variety, is analogous to that of brown coals. This is evidence of the unified trend of natural processes that are involved in the transformation of polygenous hydrocarbon raw materials and are governed by physicochemical conditions. Based on their quantitative XRD characteristics (Table 4), all the studied specimens of oxycerites belong to the brown-coal stage of catagenesis (Korolev, 1989).

We suggest that the final product of transformation of both oxycerites and brown coals will be graphite. In this case, the transformation of these compounds at different stages will be also accompanied by the release of gaseous and liquid carbon products.

Ozocerites. According to Muratov (1970) ozocerite is a result of crystallizational differentiation of petroleum and is a waxlike product most frequently of an essentially paraffin composition with a density less than 1 g cm^{-3} and $\text{H/C}_{\text{at}} \sim 2$. The consistency of ozocerites can be either soft or solid and depends on the relationship between the paraffin, oil, resinous, and asphaltene fractions.

The first results of an XRD investigation of ozocerites are reported in Atanasyan *et al.* (1982) and Korolev (1982). In order to establish the phase composition, six specimens of ozocerite from different deposits were studied. The QXPA results, as well as the d_{002} values for the predominant paraffin component, are presented in Table 5, while Fig. 6 depicts the diffraction spectra of some ozocerite samples.

All the ozocerite varieties investigated are characterized by an unequal paraffin content, whose concentration varies between 15 and 88%. The predominant paraffin component belongs to high-molecular-weight varieties (from C_{32} to C_{41}). The amorphous part consists

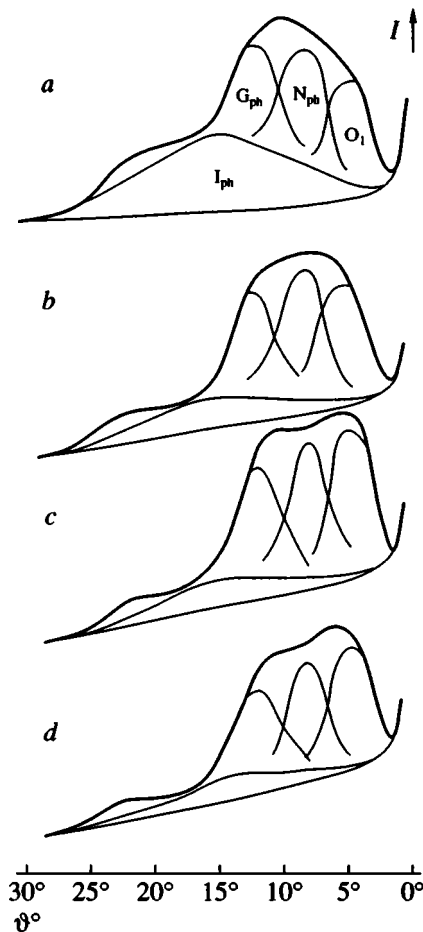


Fig. 5. Diffraction patterns of oxycerites. (a) Anadyr, Ol'khovskaya area, well 1, depth 500 m, fracture zone; fibrous oxycerites from pegmatites of the Volyn region, depth 80 m: (b) coarse-fibrous; (c) fibrous; (d) fine-fibrous.

mainly of N_{ph} with an insignificant G_{ph} impurity. The latter is connected with the presence of resinous and asphaltene constituents. Therefore, ozocerites represent a homogeneous mixture of high-molecular-weight

Table 4. Data of QXPA and chemical analysis of oxycerites and fibrous oxycerite

no.	QXPA, %					Element composition, %				
	I_{ph}	O_1	N_{ph}	G_{ph}	$G_{\text{ph}}/N_{\text{ph}}$	C	H	N	S + O	H/C_{at}
1	39	5	38	18	0.47	68.33	5.07	0.52	26.13	0.89
2	35	13	35	17	0.49	—	—	—	—	—
3	38	5	35	19	0.54	70.01	5.60	1.16	23.22	0.96
4	55	8	20	17	0.85	70.63	6.52	22.85		1.10
5	34	6	32	28	0.88	—	—	—	—	—
6	32	6	31	31	1.00	67.40	5.72	0.78	26.02	1.00
7	32	13	32	23	0.72	60.38	7.06	8.79	23.75	1.40
8	24	16	34	26	0.77	62.61	6.67	8.92	21.77	1.28
9	13	19	40	28	0.70	62.29	6.23	8.89	22.57	1.20

Note: (1–6) oxycerites; fibrous oxycerite: (7) coarse-fibrous, (8) fibrous, (9) fine-fibrous; (—) no data.

Table 5. The XRD characteristics of ozocerites

Deposit, age	Phase composition, %			d_{002} , Å	Paraffin (C_nH_{2n+2})
	paraffins	N_{ph}	G_{ph}		
Cheleken Peninsula, MZ	15	80	5	—	—
Sol-Rokho, MZ	51	43	6	53.9	$C_{41}H_{84}$
Shor-Su, no. 376, MZ	57	39	4	44.1	$C_{33}H_{68}$
no. 377	60	33	7	48.0	$C_{36}H_{74}$
no. 76	75	21	4	46.1	$C_{34}H_{70}$
Borislav, MZ specimen. 1	78	17	5	42.5	$C_{32}H_{66}$
MZ specimen. 3	83	14	3		
MZ specimen. 4	87	10	3		
MZ specimen. 2	88	10	2		

paraffin, naphthene, and amorphous graphite components.

We should also dwell on the diagnostics of naphthides. Certain authors (Melkov and Sergeeva, 1990) assume that, the based on element composition, chemical properties, and even mineralogy, many representatives of this genetic series, such as anthraxolites, kerites, and asphaltenes, can only with difficulty be distinguished from anthracites, hard coal, and brown coal,

respectively. Therefore, these authors believe that naphthides and fossil coals should be distinguished by the aggregate of geological data, such as the conditions and forms of occurrence, parageneses, interrelations with other minerals, and host rocks.

However, on the basis of the results discussed above it is possible to believe that many naphthide representatives, e.g., asphalts, asphaltites, kerites, and anthraxolites, can be readily identified by QXPA data, since their diffraction spectra do not contain the reflection with $d \approx 20$ Å corresponding to one more hydrocarbon components, which is in turn a characteristic indicator of humus hard coals of high stages and anthracites (Korolev, 1989).

As for oxycerites with an XRD composition identical to that of brown coals, geological and paragenetic indicators should be used to establish their genetic type.

Therefore, XRD analysis allows us to determine the genetic type of natural organic substances and establish the level of catagenetic transformation of organic matter in vitrinite-free geological formations.

CONCLUSION

Thus, in the process of catagenetic transformations naphthides pass through several stages. The transformation of naphthides, as other natural polygenous organic substances (Korolev, 1989; Korolev *et al.*, 1990), is connected with carbonization in chemical terms and with graphitization in structural terms. Carbonization results in the destruction of hydrocarbon components. Owing to the disproportionation of hydrogen, a part of these products promotes the origination of free carbon that is transformed into the graphite phase. Subsequently, after destruction of the hydrocarbon phases and evacuation of the destruction products, only one graphite phase remains, which transforms from the amorphous into the crystalline state (graphite) under the effect of thermal, temporal and catalytic factors. This stage is accompanied by an abrupt increase in L_{csr} (>500 Å) and a decrease in d_{002} to 3.35 Å.

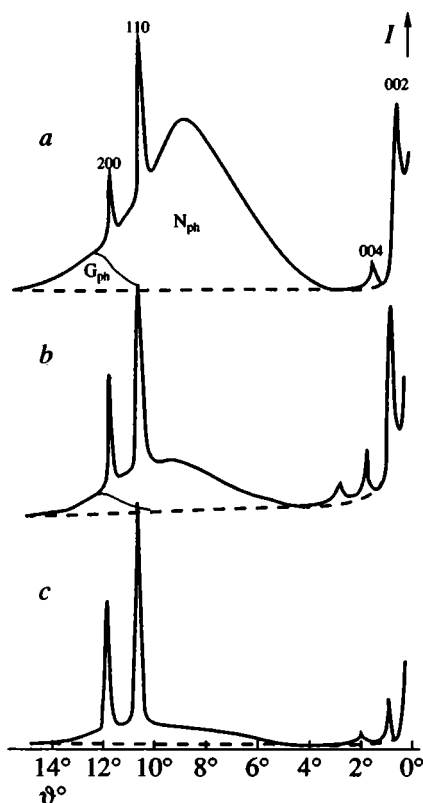


Fig. 6. Diffractograms of ozocerites. (a) Cheleken Peninsula, MZ; (b) Shorsu River, Fergana, MZ; (c) Borislav deposit, MZ.

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BOOK REVIEW

“Placer Deposits of Russia and Other CIS Countries” (*Rossyynnye mestorozhdeniya Rossii i drugikh stran SNG*)

In 1997, Nauchnyi Mir published the book *Placer Deposits of Russia and Other CIS Countries: Mineralogy, Commercial Types, Strategy of the Mineral and Raw-Material Base Development*; it was dedicated to the 85th anniversary of the Chairman of the Scientific Council on Ore-Formation and Metallogeny, Academician of the RAS N.A. Shilo. Its authors are placer specialists well known in Russia and abroad: N.G. Patyk-Kara, I.Z. Bykhovskii, B.I. Benevol'skii, P.B. Zubkov, and others, who together comprise the 13 authors. It should be noted that the necessity for publishing such a work has long been necessary, as a vast volume of data on placer deposits was scattered in numerous publications, making it difficult to use them. In the current conditions, interest in placers, distinguished from primary sources by more advantageous technical and economical characteristics, has increased still further. The monograph in question is a valuable handbook, which not only contains detailed information on placer deposits of concrete mineral resources (gold; platinum minerals; diamonds; rare, nonferrous, and ferrous metals; jewelry and ornamental stones; mining and chemical raw materials), but also considers the conditions of placer formation and regularities in their location within the crustal structures, i.e. those criteria, on which the prediction of placer provinces, groups, and regions are based.

The basic text of the monograph is preceded by sections which discuss the problems typification of placer areas and industrial classification of deposits, as well as the processes participating in the formation of valuable mineral deposits. It is noted that the total number of minerals capable of accumulation in placers exceeds fifty. Of these, about thirty-five are found in commercial-grade concentrations, but only about twenty-five minerals form deposits of their own mineral species; the rest are either present in the form of associated components or constitute a part of complex placers. The constants of hypergene stability (K_{hs}) (according to N.A. Shilo) are given for the major placer-forming minerals. This parameter determines the behavior of minerals at different stages of the placer formation. It is emphasized that the mechanisms of transposition and concentration of the size-variable placer-forming components differ substantially. Gravitational diffusion, segregation, migration-residual, and migration mechanisms of concentration of placer-forming minerals are at work in the aqueous alluvial medium alone. Moreover, the notion itself about placers as accumulations of

most stable allothigenic minerals, exclusively formed due to mechanical transposition, has changed in recent years. The authors cite the data testifying a geochemical evolution of placers, when, along with clastogene minerals, concentrations of fine-dispersed and mobile forms of various compounds are developed.

Based on the conditions of supply, specific features of concentration of useful components, and the character of placer-forming process, the authors along with many other investigators, distinguished two large genetic types of placers: proximal (autochthonous) placers and distal (allochthonous) placers. The book highlights several aspects of placers: settings and formation mechanisms, favorable conditions for the preservation in the fossilized state, geomorphological features of formation, and the belonging to various sedimentary formations. It is noted that the proximal placers can also be formed against the background of rapid renewal of the exposition, although the peneplanation of territories and the processes of chemical weathering are most important placer-forming factors. A very capacious and informative table, characterizing a relative industrial significance of placers of various genetic types and mineral species, is included in the book.

However, adhering to the classical ideas about the genesis of placers, the authors did not consider the whole spectrum of situations arising during their formation. The two genetic groups of placers, characterized in the book, are only extreme, “pure” cases in the formation of deposits. The impression may be given that by using the complex of indicators, illustrated in the monograph, it is possible to determine in each specific case the genetic assignment of a certain placer. In fact, the picture looks much more complicated, since the combination of different variants is more diverse in real conditions. In the process of peneplanation of the ore-bearing territory, the placer-forming processes are gradually transposed towards primary sources. Therefore, a certain zonality in the location of placers of various genetic types is formed even within the limits of one denudation–sedimentation cycle. In this case, the process responsible for the formation of useful mineral deposits in the accumulation areas is smoothly replaced by the formation of the distal, intermediate, proximal, and nearest placers along the ways of clastic material migration. These situations are possible when placers, redeposited near primary sources, will carry the indicators typical to those of the distal placers. Problems such as the distance between terminal basins and primary

sources, the existence period of the basin's stable coastal line, and the formation of some genetic and dynamic placer types at the expense of others are virtually not analyzed in the monograph.

In the second section of the book the authors discuss the principles of typification for placer-bearing areas, consider the series of placer formations and types of placer provinces, give the examples of placer region models, and substantiate the fundamentals for the industrial classification of placer deposits. Viewing placers as a product of relief-forming processes, the authors distinguish the following placer formations: growing mountains, disintegrating mountains, peneplains (denudation and denudation-accumulative plains), depressions, and troughs with the subformations of intracontinental, pericontinental, and shelf troughs. It is shown that the appearance of a certain placer formation is determined by a set of inherent morphogenic placer types. In the typification of placer provinces, the authors think it reasonable to distinguish the series of placer formations with respect to crustal sites with a certain type of endogene mineralization, character of tectonic and geomorphological evolution, assemblages of mineral species, and a combination of placer formations. Based on the principles of mineragenic regionalization, i.e., assignment of the territory to a certain type of the crustal structure, formulated by A.D. Shcheglov, and applying the concepts of classical tectonics about the principal structural elements of the lithosphere, the authors distinguish the following series of placer formations: geosynclinal, orogenic epigeosynclinal, orogenic epiplatformal, and platformal. All this is open to argument, however, these series should be evidently regarded as conditional, since the main principle of typification, judging from the text, is not based on a certain tectonic hypothesis, but infers a complex analysis of all known (and possible) placer-forming formations and placer-bearing levels for a concrete type of structures with due regard for the dynamics of variations in tectonic, geomorphological, lithodynamic, and facial settings of deposit formation.

Considering the fundamentals for industrial classification of placer deposits, the authors rightly note that one of the leading classification criteria and often the main one, in the industrial typification of many monomineral placer deposits (gold, tin, cinnabar, rare metal, piezoquartz, and diamonds) are the conditions of their occurrence (i.e., the morphogenic type), since *the specific features of structure and evolution of the collector, which determine the conditions of concentration and preservation of a useful mineral, are the most*

essential factors for the origination of a placer of any scale and morphology (p. 53). Knowing the leading role of a factor in the formation of deposits and in the determination of commercial value of placers, belonging to a specific group, makes it possible to predict the presence of new prospective, recoverable, and commercial (according to the author's classification) deposits.

The majority of the book is a description of placer deposits containing many kinds of mineral resources (gold, platinum, diamonds, tin, titanium, zirconium, jewelry and ornamental stones, etc.). The description of the most important commercial and recoverable types of placers, belonging to each raw-material group and mineral class, is given with evidence from concrete deposits, which play a leading role in the structure of reserves and with due regard for the prospects. Despite the fact that the book title includes only placers of Russia and other CIS countries, the authors use the examples of objects situated in other countries and regions of the world in order to more clearly characterize commercial types of deposits and illustrate their features. Here, the authors stress that the majority of placer provinces are polymineral. This is displayed in the complicated spatiogenetic relationships (ranging from the spatial superposition to close paragenetic interrelations of useful minerals) in placers of various mineral species.

The task, according to the authors, is to demonstrate the raw-material, mineral, and morphogenetic diversity of placers, to identify the most important known and prospective types of deposits, and to show the character of their localization within the crustal structures in order to predict new placer-bearing areas. This task has been accomplished. The book is written clearly, simply, and professionally. Each section ends with a comprehensive conclusion. The work is abundantly illustrated by figures, schematic maps, graphs, and tables, all in an excellent format. Thus, the problems stated are clearly understood. The bibliography alone can be used as a fine resource. This work will undoubtedly become a reference book for specialists working in fields of geology, prospecting, exploration, assessment, and development of placer deposits, as well as for lecturers, postgraduates, and students of technical schools and institutes specializing in geology and exploration. The work under consideration deserves to be nominated for one of the most prestigious prizes in the field of ore formation and minerageny.

N. N. Zinchuk and V. T. Podvysotskii

CHRONICLE

Activity of the Scientific Council for Geochemistry and Cosmochemistry, Russian Academy of Natural Sciences (RANS)

The Scientific Council for Geochemistry and Cosmochemistry was organized as a part of the Earth Science section, Russian Academy of Natural Sciences (RANS) in late 1994. Academician of the RANS, Prof. V.N. Kholodov, Dr. Sci. (Geol.–Min.), was appointed Chairman, Academicians of the RANS B.P. Zolotarev and N.A. Ozerova, as vice-chairmen, and V.A. Eroshchev-Shak (Dr. Sci.), the scientific secretary.

Academicians of the RANS V.A. Alekseenko (Krasnodar), A.A. Beus[†] (Moscow), I.G. Ganeev (Moscow), S.V. Grigoryan (Moscow–Yerevan), V.A. Zharikov (Moscow), L.N. Kogarko (Moscow), A.I. Perel'man[†] (Moscow), V.P. Fedorchuk (Moscow), A.A. Yaroshevskii (Moscow), and Corresponding Members of the RANS V.I. Vinogradov (Moscow), S.G. Neruchev (St. Petersburg), Yu.L. Pushkarev (St. Petersburg), N.L. Shilin (Moscow), Ya.E. Yudovich (Syktyvkar) were elected of the council.

The objective of the council's activity consists of the discussion and popularization of new ideas in geochemistry, cosmochemistry, lithology, as well as the science on sedimentary mineral resources, the search for new promising lines of investigation in this field, and the elaboration of methodological basis in geological and geochemical studies.

In addition to the council members, the scientists skilled in geology, geochemistry, geology of ore deposits, mineralogy, stratigraphy, paleontology, oceanology, biology, and planetology were invited to participate in seminars of the Scientific Council. The joint sessions of the Scientific Council of the RANS and the Lithological Colloquium of the Geological Institute (GIN) of the Russian Academy of Sciences (RAS) were conducted during the discussions of lithological problems (deputy director of GIN Yu.O. Gavrillov was the chairman of the Lithological Colloquium).

Researchers from many scientific institutions of the RAS, educational and applied organizations, such as the Geological Institute (GIN), Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Institute of Lithosphere (IL), Institute of Oceanology (IO), Institute of Mineralogy (IM), Paleontological Institute (PIN), All-Russia Research Institute of Mineral Resources (VIMS), State Institute of Mining and Chemical Raw Material (GIGKhS), Insti-

tute of Geochemistry and Analytical Chemistry (GEOKhI), Institute of Geology and Mining of Combustible Minerals (IGRGI), Central Astrophysical Observatory (TsAO), Moscow State University (MGU), Gubkin State Academy of Oil and Gas (GANG), Dubna International University, the Journal *Priroda*, etc. took part in meetings where topical problems were discussed.

The reports of Academician of the RANS A.A. Yaroshevskii (*Mean Chemical Composition of Magmatic Material of the Earth's Crust*) and Corresponding Member of the RANS G.B. Naumov (*Principles of Ore-forming System Analysis*) were discussed in 1995.

The reports of Academician of the RAS and RANS G.A. Zavarzin (*Geospheric–Biospheric Approach to the Biosphere Evolution*) and Academician of the RANS V.N. Kholodov (*Lithological and Geochemical Indicators of the Biosphere Evolution*) were discussed at the Council meetings in 1996.

Finally, in 1997–1998, reports of Yu.M. Malinovskii (Dr. Sci.), academicians of the RANS E.A. Romankevich and G.N. Baturin, Academician of the RAS N.P. Yushkin were presented and discussed.

In the report *Specific Geochemical Features of Biospheric Rhythm Phases* based on emission spectroscopy data, Yu.M. Malinovskii (IL) demonstrated regularities in accumulation of chemical elements exemplified by Cretaceous deposits in Siberia. The periodic accumulation of biophile and clastophile chemical elements was established, and the causes of their variations were suggested. The author referred the biospheric rhythms to cosmochemical events and to the action of natural biogenic concentrators. He emphasized the advanced formation of lithochemical indicators, relative to the biotic characteristics commonly adopted for stratigraphic purposes.

Academician of the RANS V.T. Frolov, M.A. Levitan (Dr. Sci.), M.A. Zharkov (Dr. Sci.), Yu.O. Gavrillov (Ph. D.), Yu.G. Tsekhovskii (Dr. Sci.), and Academician of the RANS V.N. Kholodov participated in the discussion. Summarizing this discussion, V.N. Kholodov has noted that the lithological events are in many aspects related to biospheric processes. The complication in research of these interrelations is caused by an incomplete lithological chronicle and intense secondary alteration of sedimentary rocks. Traces of biospheric rhythms in stratosphere are frequently obliterated, and their deciphering requires a complex analysis.

[†] Deceased.

The report *Carbon Flows and Masses in the Ocean* presented by E.A. Romankevich (IO) was based on the study of considerable factual material characterizing the regular distribution of organic and inorganic carbon in waters, suspensions, and recent sediments of the World Ocean. The author called attention to the behavior of polygenous organic matter and its burial in bottom sediments of various facies and climate zones. Maps depicting the carbon distribution in oceanic waters and sediments were demonstrated. The inorganic carbon was investigated mainly in carbonate deposits. Romankevich attempted to calculate the carbon balance covering the entire range from generation to accumulation zones. He argued that the precise balance of this component is impossible to calculate. However, the carbon cycles in various systems, including the mantle degassing, the secondary metamorphogenic degassing, the CO₂ generation during the biota vital activity, the breakdown of biota, etc. should be studied.

Many problems were touched in this report, and were the subject of lively discussion. Major questions were related to the balance of organic and inorganic carbon and the role of specific carbon forms in it. In particular, the volume of carbon exhalation supply during volcanic processes in spreading zones is currently controversial. The amount of secondary carbon introduced into sedimentary rocks in subduction zones, the amount of carbon related to the biota mineralization at geochemical barriers, etc. also remain uncertain. Academicians of the RANS O.G. Sorokhtin, A.A. Yaroshetskii, V.N. Kholodov, A.Yu. Levin (Dr. Sci.) and S.P. Perov (Dr. Sci.) participated in the discussion.

The report *Phosphate Deposition in Ocean* presented by G.N. Baturin (IO) was a generalization of the author's litho-geochemical data gained during numerous R/V cruises in different parts of the World Ocean and the review of data published by foreign oceanographers.

Baturin recognized two types of the present-day phosphate deposits: the granular deposits at shelves and the stratal-crustal deposits at seamounts and guyots. The formation of phosphate deposits of the first type was considered to be a result of upwelling following the Kazakov-Baturin model and the subsequent concentration of phosphate grains due to the sediment rewashing.

The REE distribution in phosphorites from guyots indicates that the phosphate deposits that were formed in a relatively shallow-water environment subsequently subsided to a significant depth along with seamounts and guyots. Baturin believes that the phosphorus in the current sedimentary cycle is supplied into the ocean from continents as a suspension, and is then transformed into soluble forms by plankton and accumulated due to its redistribution by upwellings. The hydrothermal supply of phosphorus in seas and oceans is negligible. The report attracted a great interest and was discussed by academicians of the RANS A.S. Sokolov, V.N. Kholodov, I.M. Varentsov (Dr. Sci.), I.O. Murdmaa (Dr. Sci.), E.L. Shkol'nik (Dr. Sci.), and others.

In conclusion, V.N. Kholodov emphasized that the new data on phosphorus geochemistry compel to reject the hydrothermal source of its supply into seas and oceans. The phosphorus is not a typical element both of the present-day hydrothermal rift systems and the hydrothermal deposits at continents. Hydrothermal phosphate occurrences are rare and, hence, their contribution to the total balance of this element is insignificant.

The report from Academician of the RAS N.P. Yushkin (*Concept of Hydrocarbon Crystallization of Life*) was focused on a possibility of abiogenic origin of protein aminoacids. The author has studied natural bitumoids (asphaltite and gilsonite) related to the oil from the Timan-Pechora region, the hydrothermal bitumoids (kerite and anthraxolite) from base metal, massive sulfide copper, and uranium deposits, and the solid hydrocarbons in shungites from Karelia and Yakutia. Special attention was called to kerites from the Ukrainian Shield pegmatites, which were suggested to be formed at high temperature and pressure ($T = 500\text{--}280^\circ\text{C}$, $P = 20\text{ MPa}$).

As was shown, the composition of natural bitumoids regularly varies from low- to high-temperature naphthides. The aminoacid content increases and its spectrum is slightly altered in the same direction. The aminoacid composition in high-temperature shungite and fibrocrySTALLINE kerites drastically differs from similar components of naphthides. The SEM study has shown that the carbonaceous material of high-temperature bitumoids is strongly structurized and is represented by fibrous, spheroidal, fullerine and spiral species resembling many biogenic structures of bacterial-algal origin.

The author concluded that the physicochemical environment of the pegmatite formation creates all conditions, which are required for the abiogenic aminoacid synthesis, including the favorable gas medium (ammonia, sulfuric gases, carbon dioxide, methane, etc.), sources of energy, and the presence of catalysts. Thus, the formation of pegmatites could be accompanied not only by an abiogenic aminoacid synthesis, but also by a self-assembly of proteins and even by the development of those inherent to organism functions, which are commonly regarded as biological. He proposes a new model of creation for the protobiological organism that is inferred to be a precursor of all forms of life.

Yushkin's report attracted a great interest and was discussed by Academician RAS G.A. Zavarzin, Corresponding Member RAS P.P. Timofeev, Academician of the RANS V.N. Kholodov, V.M. Gorlenko (Dr. Sci.), V.V. Bugrovskii (Dr. Sci.), Yu.O. Gavrilov (Dr. Sci.), and others.

The Scientific Council for Geochemistry and Cosmochemistry invites all specialists in geochemistry, lithology, stratigraphy, biology, paleontology, geology of ore deposits, and petrography to participate in its meetings.

**V.N. Kholodov, B.P. Zolotarev,
and V.A. Eroshchev-Shak**

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The reports of Academician of the RAS and RANS G.A. Zavarzin (*Geospheric–Biospheric Approach to the Biosphere Evolution*) and Academician of the RANS V.N. Kholodov (*Lithological and Geochemical Indicators of the Biosphere Evolution*) were discussed at the Council meetings in 1996.

Finally, in 1997–1998, reports of Yu.M. Malinovskii (Dr. Sci.), academicians of the RANS E.A. Romankevich and G.N. Baturin, Academician of the RAS N.P. Yushkin were presented and discussed.

In the report *Specific Geochemical Features of Biospheric Rhythm Phases* based on emission spectroscopy data, Yu.M. Malinovskii (IL) demonstrated regularities in accumulation of chemical elements exemplified by Cretaceous deposits in Siberia. The periodic accumulation of biophile and clastophile chemical elements was established, and the causes of their variations were suggested. The author referred the biospheric rhythms to cosmochemical events and to the action of natural biogenic concentrators. He emphasized the advanced formation of litho-geochemical indications, relative to the biotic characteristics commonly adopted for stratigraphic purposes.

Academician of the RANS V.T. Frolov, M.A. Levitan (Dr. Sci.), M.A. Zharkov (Dr. Sci.), Yu.O. Gavrilo (Ph. D.), Yu.G. Tsekhovskii (Dr. Sci.), and Academician of the RANS V.N. Kholodov participated in the discussion. Summarizing this discussion, V.N. Kholodov has noted that the lithological events are in many aspects related to biospheric processes. The complication in research of these interrelations is caused by an incomplete lithological chronicle and intense secondary alteration of sedimentary rocks. Traces of biospheric rhythms in stratosphere are frequently obliterated, and their deciphering requires a complex analysis.

[†] Deceased.

The report *Carbon Flows and Masses in the Ocean* presented by E.A. Romankevich (IO) was based on the study of considerable factual material characterizing the regular distribution of organic and inorganic carbon in waters, suspensions, and recent sediments of the World Ocean. The author called attention to the behavior of polygenous organic matter and its burial in bottom sediments of various facies and climate zones. Maps depicting the carbon distribution in oceanic waters and sediments were demonstrated. The inorganic carbon was investigated mainly in carbonate deposits. Romankevich attempted to calculate the carbon balance covering the entire range from generation to accumulation zones. He argued that the precise balance of this component is impossible to calculate. However, the carbon cycles in various systems, including the mantle degassing, the secondary metamorphic degassing, the CO₂ generation during the biota vital activity, the breakdown of biota, etc. should be studied.

Many problems were touched in this report, and were the subject of lively discussion. Major questions were related to the balance of organic and inorganic carbon and the role of specific carbon forms in it. In particular, the volume of carbon exhalation supply during volcanic processes in spreading zones is currently controversial. The amount of secondary carbon introduced into sedimentary rocks in subduction zones, the amount of carbon related to the biota mineralization at geochemical barriers, etc. also remain uncertain. Academicians of the RANS O.G. Sorokhtin, A.A. Yaroshevskii, V.N. Kholodov, A.Yu. Levin (Dr. Sci.) and S.P. Perov (Dr. Sci.) participated in the discussion.

The report *Phosphate Deposition in Ocean* presented by G.N. Baturin (IO) was a generalization of the author's litho-geochemical data gained during numerous R/V cruises in different parts of the World Ocean and the review of data published by foreign oceanographers.

Baturin recognized two types of the present-day phosphate deposits: the granular deposits at shelves and the stratal-crustal deposits at seamounts and guyots. The formation of phosphate deposits of the first type was considered to be a result of upwelling following the Kazakov-Baturin model and the subsequent concentration of phosphate grains due to the sediment rewashing.

The REE distribution in phosphorites from guyots indicates that the phosphate deposits that were formed in a relatively shallow-water environment subsequently subsided to a significant depth along with seamounts and guyots. Baturin believes that the phosphorus in the current sedimentary cycle is supplied into the ocean from continents as a suspension, and is then transformed into soluble forms by plankton and accumulated due to its redistribution by upwellings. The hydrothermal supply of phosphorus in seas and oceans is negligible. The report attracted a great interest and was discussed by academicians of the RANS A.S. Sokolov, V.N. Kholodov, I.M. Varentsov (Dr. Sci.), I.O. Murdmaa (Dr. Sci.), E.L. Shkol'nik (Dr. Sci.), and others.

In conclusion, V.N. Kholodov emphasized that the new data on phosphorus geochemistry compel to reject the hydrothermal source of its supply into seas and oceans. The phosphorus is not a typical element both of the present-day hydrothermal rift systems and the hydrothermal deposits at continents. Hydrothermal phosphate occurrences are rare and, hence, their contribution to the total balance of this element is insignificant.

The report from Academician of the RAS N.P. Yushkin (*Concept of Hydrocarbon Crystallization of Life*) was focused on a possibility of abiogenic origin of protein aminoacids. The author has studied natural bitumoids (asphaltite and gilsonite) related to the oil from the Timan-Pechora region, the hydrothermal bitumoids (kerite and anthraxolite) from base metal, massive sulfide copper, and uranium deposits, and the solid hydrocarbons in shungites from Karelia and Yakutia. Special attention was called to kerites from the Ukrainian Shield pegmatites, which were suggested to be formed at high temperature and pressure ($T = 500-280^{\circ}\text{C}$, $P = 20 \text{ MPa}$).

As was shown, the composition of natural bitumoids regularly varies from low- to high-temperature naphthides. The aminoacid content increases and its spectrum is slightly altered in the same direction. The aminoacid composition in high-temperature shungite and fibrocrystalline kerites drastically differs from similar components of naphthides. The SEM study has shown that the carbonaceous material of high-temperature bitumoids is strongly structurized and is represented by fibrous, spheroidal, fullerine and spiral species resembling many biogenic structures of bacterial-algal origin.

The author concluded that the physicochemical environment of the pegmatite formation creates all conditions, which are required for the abiogenic aminoacid synthesis, including the favorable gas medium (ammonia, sulfuric gases, carbon dioxide, methane, etc.), sources of energy, and the presence of catalysts. Thus, the formation of pegmatites could be accompanied not only by an abiogenic aminoacid synthesis, but also by a self-assembly of proteins and even by the development of those inherent to organism functions, which are commonly regarded as biological. He proposes a new model of creation for the protobiological organism that is inferred to be a precursor of all forms of life.

Yushkin's report attracted a great interest and was discussed by Academician RAS G.A. Zavarzin, Corresponding Member RAS P.P. Timofeev, Academician of the RANS V.N. Kholodov, V.M. Gorlenko (Dr. Sci.), V.V. Bugrovskii (Dr. Sci.), Yu.O. Gavrilov (Dr. Sci.), and others.

The Scientific Council for Geochemistry and Cosmochemistry invites all specialists in geochemistry, lithology, stratigraphy, biology, paleontology, geology of ore deposits, and petrography to participate in its meetings.

**V.N. Kholodov, B.P. Zolotarev,
and V.A. Eroshchev-Shak**

CHRONICLE

The Problem of Present-Day Phosphorite Formation

A regular session of the Scientific Council on Geochemistry and Astrochemistry, Russian Academy of Sciences, and colloquium of the Lithologic section of the Geological Institute, Russian Academy of Sciences, was held at the GIN on December 19, 1997, under the chairmanship of Academician of the Russian Academy of Natural Sciences (RANS), Prof. V.N. Chodolov, Dr. Sci. (Geol.–Min.).

The report *Phosphorite Accumulation in Oceans* by Academician of the RANS G.N. Baturin (Dr. Sci.) was heard at the session. Judging by a number of questions put and the discussion arisen, the report evoked great interest. Baturin's conclusions were based on thoroughly processed factual data. He indicated that two types of phosphorites are revealed in present-day oceans: granular phosphorites developed at shelves and stratal-crustal phosphorites at seamounts (guyots). Type 1 phosphorites were formed as a result of upwelling, when the bioproductivity outburst resulted in intense disposal of organic remains in sediments. Organic phosphorus, which was released as a result of the decay of organic remains was mineralized and became the source of formation of small phosphate nodules (grains), which were subsequently many times reworked and precipitated as phosphorite-bearing sands often representing deposits.

The report was ambiguous with respect to phosphorite genesis at guyots. At the same time, Baturin considered that the REE spectra indicated that phosphorites were formed at shallow depths and, then, submerged together with guyots. The analysis of the geochemical features of the sediments studied allowed Baturin to conclude that the traces of a volcanogenic (endogenic) source of phosphorus was absent. This opinion was not shared by some participants of the session. I.M. Varentsov, for instance, informed the group that he had observed the interbedding of ferruginous and phosphate crusts at guyots. Because, according to Varentsov, ferruginous crusts are of a hydrothermal genesis, one cannot rule out that hydrotherms also influence the phosphate component of these crusts.

I.O. Murdmaa assumed that phosphorites could be formed as a result of endo-upwelling, i.e., penetration of sea waters into seamount rocks, subsequent heating of these waters, and their convective upwelling. It is supposed that a solution formed in such a manner becomes enriched in phosphorus, which then precipitates on the surface as calcium phosphate.

A.S. Sokolov remarked upon a number of theoretical problems of phosphate geology some of which were

not discussed by Baturin. Sokolov dwelt on these aspect in the report *Phosphorus in the Stratosphere* on a similar session on February 15, 1995. He defended the concept of volcanogenic source of phosphorus, explaining this by the fact that volcanism on the Earth was more intensive and therefore, phosphorus generation was more extensive in the ancient epochs than in the Quaternary. Sokolov also dwelled upon the evolution of mineral composition of phosphorites on the basis of the CO₂ content of phosphate minerals. This problem was ignored in Baturin's report because it has been thoroughly studied and elucidated in the papers and monographs by V.Z. Bliskovskii, Yu.N. Zanin, G.N. Baturin, and many others. According to these researchers, the content of CO₂ indeed varies in different types of phosphorites: 5–6% in Jurassic–Cretaceous rocks (nodular), 3–4% in Cretaceous–Paleogene rocks (granular), and above 6% in present-day phosphorites. At the same time, the works of R.G. Knubovets *et al.* indicated that the isomorphic series of francolites can vary from kurskite to fluorcarbonate-apatite, fluorapatite and hydroxylapatite depending on thermodynamic conditions of catagenesis governed by regional (or contact) metamorphism, host rock composition, weathering, and other factors.

Based on specific examples of present-day oceanic phosphorites, V.Z. Bliskovskii had previously indicated that fluorcarbonate-apatite is formed as a result of exothermal recrystallization of a kurskite-type mineral at temperature of 500°C. In the above works, it has been shown that the primary mineral composition of phosphorites does not change, and its compositional variations are explained by postdiagenetic processes. The same inference is valid for Sokolov's statement about the evolution of uranium content. According to Sokolov, the uranium content is 10 ppm in Cambrian phosphorites, 100 ppm in Cretaceous phosphorites, and up to 150–200 ppm in Miocene–Pliocene phosphorites. This example does not illustrate the evolution of a phosphate mineral, but once more points to the long known and well-studied high migration capacity of uranium.

In appraising Baturin's report, Sokolov mentioned that, as an applied geologist, he attaches no economical significance to the objects considered, because he believes that these are very wide spread phosphate-bearing rocks rather than phosphorites. One can hardly agree with such a statement for two reasons. First, Baturin's monograph and his numerous publications are rich in chemical analyses, from which it can be derived that only phosphorites, i.e., the rocks with 13–

18% and higher P_2O_5 content (according to different classifications) were studied. Sokolov apparently kept in mind phosphorite ores rather than phosphorites. Second, proceeding from Sokolov's position, phosphate-bearing rocks of the Baltic region and Russian Platform should not be a matter of interest to applied geologists, but they have been developed for many decades, because technological properties and feasibility of ores, which are independent of P_2O_5 content, are, first of all, of practical interest. This is well illustrated by unfeasible Malyi Karatau phosphorites (P_2O_5 up to 20%), which are used in road paving, in contrast to the Baltic region phosphate-bearing rocks (P_2O_5 7–10%), which have been exploited for many years. Taking into account the above said, I support Baturin's opinion that oceanic phosphorites are very prospective, because large phosphate sand deposits (4 Gt with P_2O_5 up to 25–30%) have been explored and prepared for exploitation in Namibia.

G.Yu. Butuzova, who studied present-day hydrothermal-sedimentary oceanic ore formation, strongly criticized the concepts of hydrothermal source of phosphorus. She mentioned that the studies, carried out within the global system of rift zones of the World Ocean, indicated that phosphorus contents are very low and nearly absent, in both hydrothermal solutions and in related various ore manifestations. Thus, Butuzova

suggests that the scale of this phenomenon cannot affect its essence.

Summing up the discussion, chairman of the session Kholodov, expressed his opinion on certain disputable problems. He mentioned that the hypothesis of hydrothermal phosphorite formation has many shortcomings. First, the phosphorus content in present-day hydrotherms and exhalations is negligible. Second, large deposits of hydrothermal phosphorites have not been discovered on the Earth, and that hydrothermal phosphate manifestations have a complex structure and ambiguous genesis. Finally, it is very problematic that the epochs of phosphorite formation coincide with the periods of high hydrothermal activity and continental rifting.

The content of uranium in phosphorites is a complex problem, which can be solved only on the basis of analysis of a large body of statistical data, still not generalized.

The presented brief information about Baturin's report and the discussion arisen indicates that the problems of genesis of both present-day and ancient phosphorites are far from a final solution.

R. K. Paul

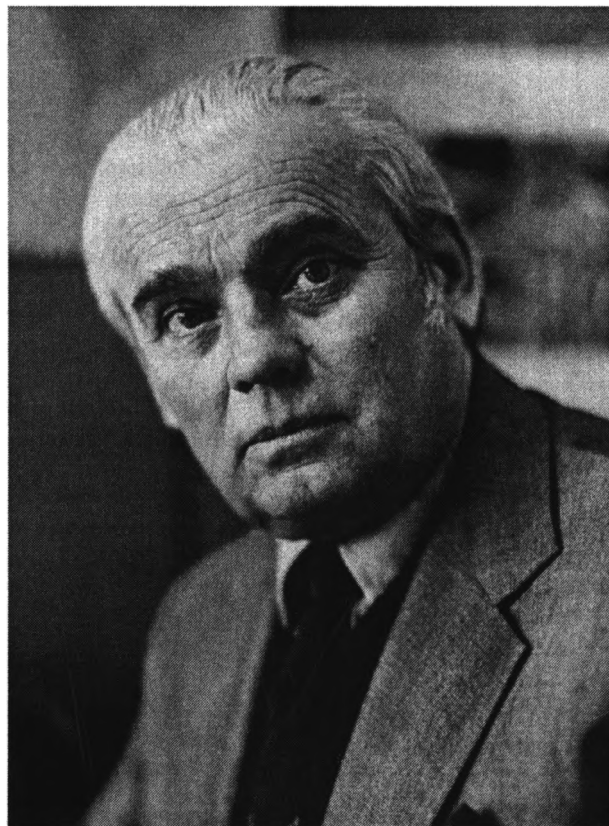
CHRONICLE

The 80th Birthday of Petr Petrovich Timofeev

On November 14, 1998 Corresponding Member of the RAS, Professor of the Lomonosov Moscow State University, Petr Petrovich Timofeev (Dr. Sci.) became 80. Timofeev is an outstanding lithologist and coal-geologist, Chairman of the Interdepartmental Lithological Committee, Counselor of the Board of directors of the Geological Institute, Russian Academy of Sciences (GIN), winner of the State Prize of the USSR, and an honorary professor of the International Science Foundation.

Timofeev carried out facial and formational investigations of the Meso–Cenozoic deposits in Tuva, Southern Siberia, Central Asia, the Urals, Caucasus, Crimea, and Ukraine, as well as the recent sedimentation and peat accumulation regions in the Rioni intermontane trough, Baltic Sea region, Cuba, and Florida (USA). These investigations formed a substantial contribution to the theory and practice of solving lithology and coal geology problems. In his monographs *The Jurassic Coal-bearing Formation of the Tuva Trough* (1964), *Geology and Facies of the Jurassic Coal-bearing Formation of Southern Siberia* (1969), and *The Jurassic Coal-bearing Formation of Southern Siberia and Conditions of Its Development* (1970), Timofeev developed a genetic approach in coal geology, proposed the method for detailed lithofacial study, and formulated the fundamentals for genetic formational analysis of coal-bearing deposits as a method for their historical and geological understanding. In subsequent publications, he demonstrated the universality of these methods and their applicability to the whole complex of sedimentary formations.

Timofeev's works on the formational analysis in many respects developed the ideas of the founders of this method (Academicians N.M. Strakhov and N.S. Shatsky, Corresponding Member of the RAS Yu.A. Zhemchuzhnikov), as well as other outstanding scientists. He regards the term *formation* as a genetically governed geological body, connected with a certain tectonic structure and evolutionary stage of a region. Applying the lithofacial and formational methods of analysis, Timofeev revealed the details of genetic interrelations of many geological phenomena typical for the Jurassic coal-bearing formation of Southern Siberia. He proposed a new correlative stratigraphic scheme of Jurassic deposits in this region, reflecting the stage-by-stage development and the specific structural features of rock formation in separate parts of Southern Siberia. The establishment of four (deltaic–littoral, deltaic, fluvial valley, and lacustrine) types of peat accumulation was basically an important moment of both theoretical and



practical significance for the assessment of coal potential and planning of exploratory works. The investigations of Siberian coal-bearing sequences formed the basis for his Dr. Sci. dissertation, which was defended in 1967. In 1972 he was honored with the State Prize of the USSR.

Timofeev's pioneer proposal considering the coal bed as a stage of coal-bearing formation development was based on concrete scientific data. Using the example of coal-bearing deposits in the Donbass region, he revealed the relationship of the genetic types of coals with the paleogeographic–paleotectonic environments of sedimentation and peat accumulation, which subsequently was confirmed on other coal-bearing formations in the USSR and foreign countries (USA, Germany, Great Britain, France, Belgium, etc.) and formed the basis for elaboration of principles for the genetic classification of humus coals.

The first in world genetic classification of humus coals of the USSR was elaborated by P.P. Timofeev with the participation of L.I. Bogolyubova, and is

adopted by The International Committee on Coal Petrology as *The System of the Geological Institute, Academy of Sciences of the USSR, Moscow* for the classification of coals. This classification represents a system, in which each coal type is distinguished by the structure of organic matter, thus occupying a certain place in it. Needless to say, its genesis depends on a combination of paleogeographic and paleotectonic settings of sedimentation and peat accumulation.

The complex of investigations on coal-bearing deposits allowed to Timofeev to predict the prospects for reserve increase in a number of coal deposits. The predictions were confirmed by drilling in the Ulugkhan Basin (Tuva), as well as in the Tkvibuli-Shaor (Georgia) and Izhdivan (Armenia) deposits.

During the last years, Timofeev has focused his scientific activities on three problems: evolution of oceans, energetics of the sedimentary process, and development of the genetic science about geological formation.

The investigations, carried out in accordance with the program *The World Ocean*, are of special interest. Based on the analysis of materials from 100 boreholes of deep-water drilling in the Atlantic Ocean's sedimentary cover, P.P. Timofeev in cooperation with V.V. Ere-meev concluded that during the evolution of this basin, shallow-water environments were gradually replaced with deep-water ones, and the oceanic stage proper in the existence of free hydrosphere develops only during the post-Cretaceous time. A more general conclusion that the present-day oceans represent terminal basins, which appeared only at late stages of the Earth's evolution, was drawn by P.P. Timofeev in cooperation with V.N. Kholodov and V.P. Zverev in a series of journal papers.

In a number of recent publications Timofeev has arrived at the conclusion that the most important hypothesis, destined to integrate different directions in the geology of the 21st century, is the hypothesis of the Earth's expansion.

Timofeev gives much attention to the training of scientific personnel. His former students successfully develop lithological-genetic studies in various regions of Russia and abroad. He has supervised and consulted 25 Dr. Sci. dissertations and 37 Ph. D. dissertations.

In 1960 Timofeev was nominated deputy director and head of the Sector of Lithology and Geochemistry,

GIN. In 1985–1989 he was at first acting director and then director of the Institute of Geology, Russian Academy of Sciences.

In 1983 on the basis of the Department of Historical Geology in the Geological Faculty of the Lomonosov, Moscow State University, the Department of Lithology and Marine Geology was organized on the initiative of Timofeev and flourished due to his active participation. He was appointed the head of this department. Later, in the framework of the integration of science and higher schooling, the branch of this department was organized in the Geological Institute. Timofeev prepared for the students two courses of lecture (*The Teaching about Facies and Paleogeography* and *The Teaching about Geological Sedimentary Formations*). He published more than 380 works including 11 monographs.

Timofeev devotes much effort to management. He is the chairman of the Interdepartmental Lithological Committee and the head of its two sections, a member of two specialized academic councils, the chairman of the Lithological section of the National Committee of Geologists, a member of the Editorial board of the journal *Lithology and Mineral Resources*, and a member of the International Association of Sedimentologists.

Timofeev delivered many lectures at international geological, sedimentological, and coal congresses, as well as various international symposia, specialized commissions, etc.

For his substantial achievements in the field of geology and training of highly skilled specialists, Timofeev was awarded with the Order of the Red Banner of Labor, Order of October Revolution, and Order of Friendship of Peoples, as well as with nine medals.

Timofeev meets his anniversary in the prime of his life. The lithologists of the Institute of Geology, Russian Academy of Sciences, Interdepartmental Lithological Committee and Editorial board of the journal *Lithology and Mineral Resources* wish him health and new successes.

**Editorial Board of the Journal
Lithology and Mineral Resources
Interdepartmental Lithological Committee
Geological Institute (GIN),
Russian Academy of Sciences**

CHRONICLE

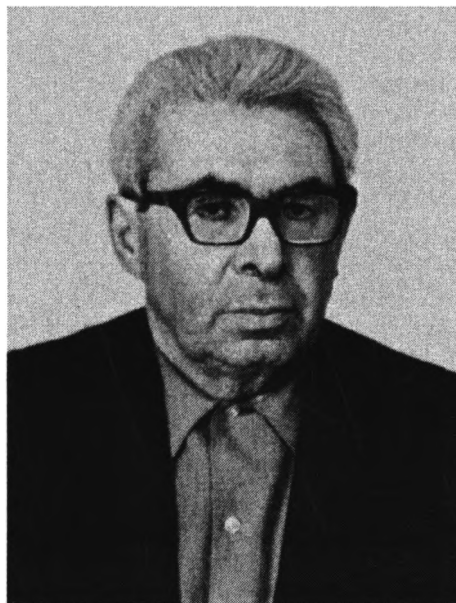
In Memory of A. I. Perel'man

Professor Aleksandr Il'ich Perel'man, Dr. Sci. (Geol.–Min.), Academician of the RANS, an outstanding geochemist, winner of the State prize of the USSR and the prize of the Russian Federation Government, and a member of the New York Academy of Sciences, passed away on March 7, 1998, at the age of eighty-two.

Perel'man graduated from the Soil and Geographic Faculty of Moscow State University (MGU) in 1938. When he was a student, the works of V.I. Vernadsky, A.E. Fersman, and B.B. Polynov and lectures of A.A. Saukov turned his interest to geochemistry, where he devoted his life. In 1941, he defended his Ph. D. dissertation *The Energy Characteristics of Certain Reactions of Chemical Weathering* under the supervision of V.V. Gemmerling. In 1953, he completed and successfully defended his Dr. Sci. dissertation based on the geochemistry of rare metals.

Perel'man was an indefatigable field explorer. Expeditions in Central Asia, Kazakhstan, Siberia, European Russia, the Urals, Caucasus, and other regions, allowed him to develop different scientific fields, such as geochemistry of supergene processes, exogenic ore formation at geochemical barriers, geochemistry of uranium deposits, landscape geochemistry, and technological geochemistry. Developing the ideas of Academician of the RAS Polynov, Perel'man worked out landscape geochemistry as an independent and integral scientific direction, defined basic branches, formulated main regularities and concepts, and determined the fields of its practical application, among which the geochemical methods of prospecting for ore deposits and environmental protection from pollution are the major ones. His classification of geochemical landscapes made it possible to compile the pioneer *Map of Geochemical Landscapes of the USSR*, which was included in the *World Physiographic Atlas* (1964), and to regionalize the USSR territory on the basis of conditions of geochemical prospecting for ore deposits. For his monograph *Landscape Geochemistry* (1966), the Geographic Society awarded Perel'man the Litke gold medal.

While studying epigenetic processes in the supergenesis zone, Perel'man came to the realization that it is necessary to classify rock alternations under the influence of groundwater as a specific natural phenomenon. Combining principles of thermodynamics with a detailed study of natural phenomena, Perel'man worked out an original geochemical classification of these phenomena. He distinguished and thoroughly described a specific gley type previously known only in soils. His studies in migration of chemical elements



with water are of special significance. Perel'man deduced the equation of migration intensity, and introduced the concept of coefficient of water migration and migration contrast. Consequently, it became possible to compare migration of common and rare elements, to characterize behavior of almost all elements of the periodic system in a landscape and the supergenesis zone. He worked out the classification of elements by their features of migration in the supergenesis zone.

His hypothesis of geochemical barriers, i.e., the crustal sections where migration intensity of chemical elements sharply changes, ore bodies are formed, and elements-pollutants are localized, is an important scientific achievement. Based on the concept of the great cycle of substances in the Earth's crust, he formulated geochemical aspects of stratisphere energetics, established the relationship between energy and intensity of ore formation, and formulated the concept of element technophily.

In his last years, Perel'man was much engaged in the problems of atomic industry from the position of landscape geochemistry. Considering geochemical landscape as a self-organizing system capable of resisting technological impact, he formulated the main law of landscape self-organization and worked out the classification of geochemical landscapes by conditions of migration of radionuclides and their concentration at geochemical barriers. This made it possible to compile his *Map of Landscape-Geochemical Conditions of*

Radionuclide Migration and Location of Atomic Industry Plants in Russia, with a scale of 1 : 4000000.

Perel'man published 320 scientific works, including 17 monographs such as *Landscape Geochemistry* (1955, 1966, 1975), *Geochemistry of Epigenetic Processes (Supergenesis Zone)* (1965, 1966, 1968), *Geochemistry of Elements in the Supergenesis Zone* (1972), *Geochemistry of Ore Province Landscapes* (1982), *Natural Water Geochemistry* (1982), *Biologically Inert Systems of the Earth* (1977), *Salt Migration at Plains of Eastern Turkmenia and Western Uzbekistan in the Neogene* (1959), *Study of Geochemistry: Science Methodology* (1987), and others. Principles of modern geochemistry, notions of the types of chemical element migration and noosphere, as well as other theoretical aspects of prime importance for solving the environmental problems are discussed in his textbook *Geochemistry* (1979, 1989), which is a basic guide for students of institutes and universities.

The problems of radionuclide contamination and their solution from the positions of landscape geochemistry are considered in the chapter "Geochemical Landscapes of Russia and Radiogeocology" in *Recent Changes in the Lithosphere under the Influence of Natural and Anthropogenic Factors* (1966). Perel'man's works have been translated into English, German, Bulgarian, Hungarian, Romanian, Polish, Chinese, Korean, Vietnamese, and Japanese.

Perel'man was much engaged in training of scientific personnel. He wrote the handbook on landscape geochemistry, which he provided for the first-year students of MGU from 1951 to 1998. He supervised more than 30 Ph. D. and eight Dr. Sci. dissertations.

History and methodology of science were prominent in Perel'man's creative activities. He is the author of scientific biographies by Fersman, Polynov, and Saukov. His popular-science books on geochemistry *Atoms in Nature*, *The Earth's Crust and the Biosphere*, *Geochemistry of the Biosphere*, *The Earth's Chemical Composition*, and others, are well known.

Perel'man attached great significance to the relationship between science and practice. The ideas and methods he elaborated upon are successfully adopted in geochemical and environmental works not only in Russia and other CIS countries but also in the United States, Canada, Germany, China, and other countries.

During the Great Patriotic War, Perel'man was an army geologist in the Spetsgeo department, he carried out geological works under the supervision of the engineering force of the Red Army at the Southern, Ukrainian, and Belorussian fronts. He was awarded the *Order of Patriotic War* (II degree) and several medals.

Due to his wide erudition, diverse scientific interests, kindness, and personal charm, Perel'man gained indisputable prestige as a man absolutely devoted to science, always ready to help any specialist interested in geochemistry. He will remain as such a man in the memory of all who knew him.

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The Staff of the Institute of Geology of Ore Deposits,
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(IGEM), Russian Academy of Sciences**

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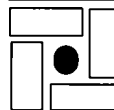
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